Organic Chemistry & Polymers -- Chapter 21 (and 12.9)

1. Introductory Topics

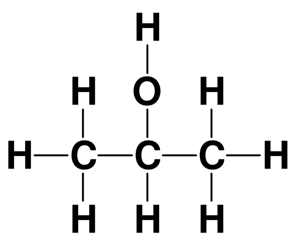
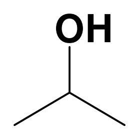
Bonding and Structure Concepts

Review Chapters 9 and 10

(especially Lewis dot formulas, VSEPR, and Valence Bond Theory)

Types of Chemical Formulas

e.g., 2-propanol (*iso*-propanol)

 ***expanded*** formula	$CH_3-CH(OH)-CH_3$ or $CH_3CH(OH)CH_3$ ***condensed*** formula	 ***fully condensed*** formula (missing C's and H's are understood)

!!! Always FOUR BONDS to Carbon !!!

Structural Isomers - same chemical formula, but different arrangement (connectivity) of atoms

e.g., C_3H_8O - 3 isomers (2 alcohols, 1 ether)

$CH_3-CH_2-CH_2-OH$
1-propanol

$CH_3-CH(OH)-CH_3$
2-propanol

$CH_3-CH_2-O-CH_3$
ethyl methyl ether

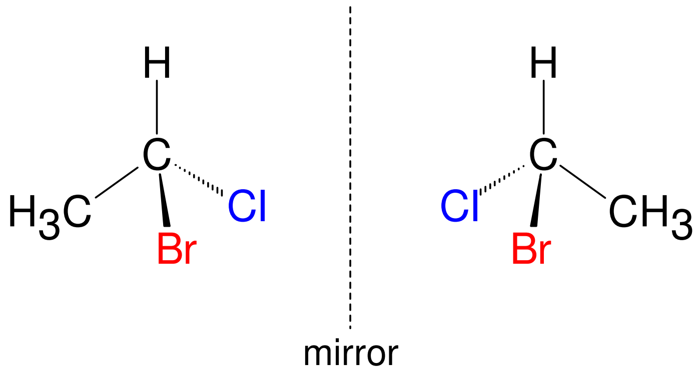
number of possible isomers can be very large, e.g.:

C_3H_8	C_4H_{10}	C_5H_{12}	C_6H_{14}	C_8H_{18}	$C_{10}H_{22}$	$C_{20}H_{42}$
1	2	3	5	18	75	> 10^5

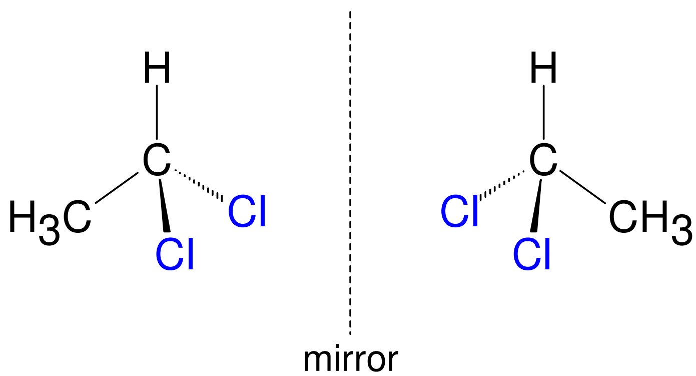
Optical Isomers (aka enantiomers)

- non-superimposable mirror images
- occur when *four different groups* are attached to a tetrahedral (sp^3) carbon center, i.e., a "chiral center"
- all physical and most chemical properties are the same but enantiomers interact differently with other chiral molecules

e.g., $CH_3CH(Br)Cl$ is chiral and exhibits enantiomers because its mirror images are not superimposable.

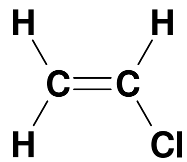


In contrast, CH_3CHCl_2 is not chiral because it is superimposable on its mirror image.

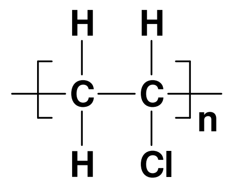


2. Organic Functional Groups

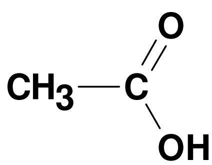
Tremendous Variety **of organic molecular structures and properties are possible, e.g.:**



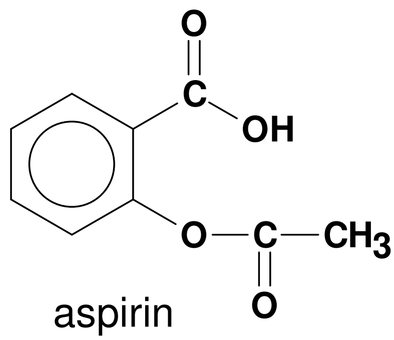
vinyl chloride



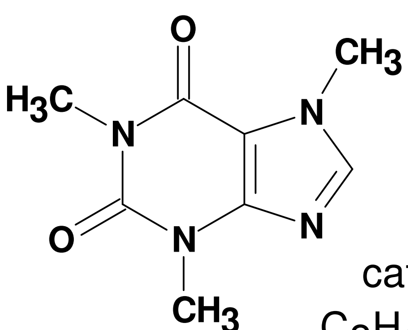
poly(vinyl chloride)
"PVC"



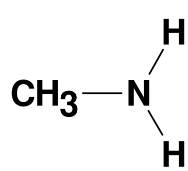
acetic acid



aspirin



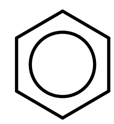
caffeine
$C_8H_{10}N_4O_2$



methylamine

***fortunately*, the subject is very *systematic* !**
and is readily classified by "organic functional groups"

Organic Functional Groups

Family	Characteristic Structural Feature	Examples
Hydrocarbons		
Alkanes	only single bonds	CH_3CH_3
Alkenes	C=C	CH_2=CH_2
Alkynes	C≡C	HC≡CH
Aromatic	benzene ring	
Alcohols	R-OH	CH_3CH_2OH
Ethers	R-O-R'	CH_3OCH_3
Aldehydes	R–C(=O)–H	CH_3–C(=O)–H
Ketones	R–C(=O)–R'	CH_3–C(=O)–CH_3
Carboxylic Acids	R–C(=O)–OH	CH_3–C(=O)–OH
Esters	R–C(=O)–OR'	CH_3–C(=O)–OCH_3
Amines: 1°	RNH_2	CH_3NH_2
2°	RNHR'	$(CH_3)_2NH$
3°	RNR'R''	$(CH_3)_3N$
Amides	R–C(=O)–N(H (R'))(H (R''))	CH_3–C(=O)–NH_2

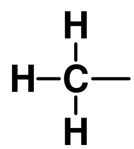
3. Hydrocarbons

(a) Alkanes C_nH_{2n+2}

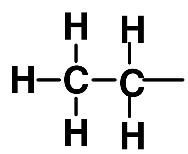
CH_4	methane	C_5H_{12}	pentane
C_2H_6	ethane	C_6H_{14}	hexane
C_3H_8	propane	C_7H_{16}	heptane
C_4H_{10}	butane	C_8H_{18}	octane, etc......

alkyl groups

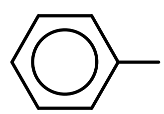
methyl CH_3



ethyl CH_3CH_2

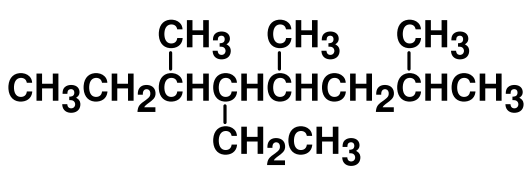


phenyl C_6H_5



***Nomenclature* of alkanes** (see book for "rules")

e.g.,



5-ethyl-2,4,6-trimethyloctane

Reactions **of alkanes** (generally unreactive)

free radical substitution (not selective!)

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$$

dehydrogenation (reverse Rx is more common!)

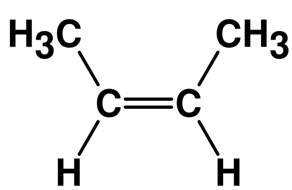
$$C_2H_6 \longrightarrow H_2C{=}CH_2 + H_2$$

"cracking" of hydrocarbons (petroleum industry)

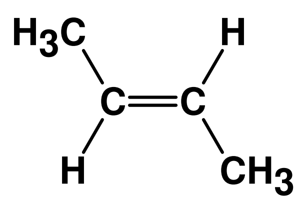
(b) Alkenes ~ C=C double bond

C_nH_{2n} (with one double bond)

Geometric Isomers are possible, e.g.:



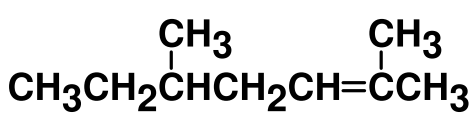
cis-2-butene



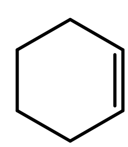
trans-2-butene

- restricted C=C bond rotation
- trigonal planar geometry at C=C carbons
- *sp*^{2} hybridization at C=C carbons

Nomenclature (C=C bond takes preference)



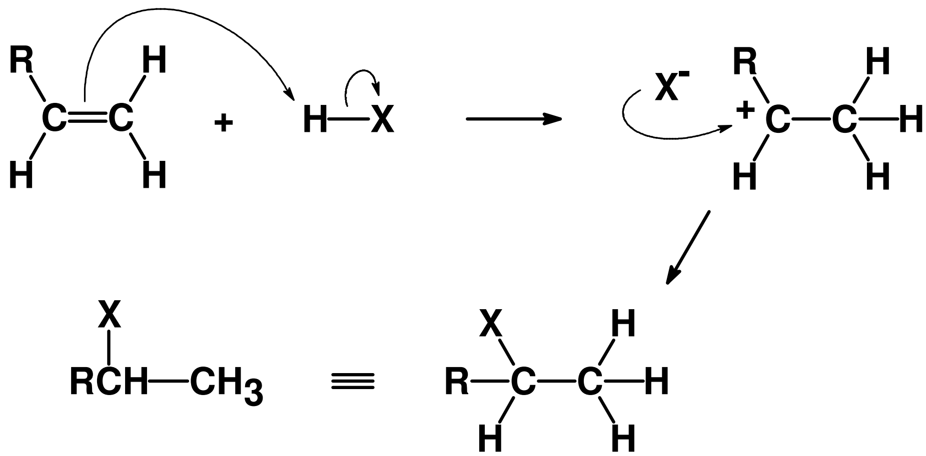
2,5-dimethyl-2-heptene



cyclohexene

Reactions of alkenes ~ *addition* to double bond

$$RCH{=}CH_2 \;+\; HX \;\longrightarrow\; RXCH\text{-}CH_3$$



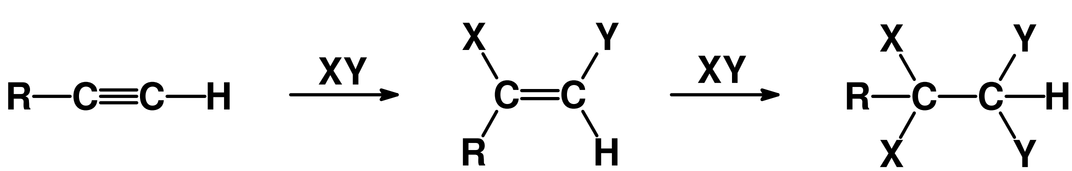
Markarnikov's rule ~ "them that has, gets"
(H goes on the C that already has the most H's)

addition of *non-polar* reagents (H_2, Br_2, etc.) also occurs

(c) Alkynes ~ C≡C triple bond

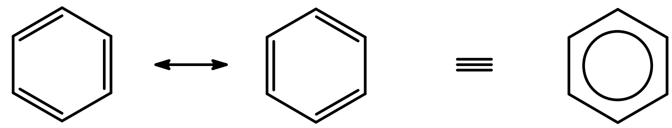
C_nH_{2n-2} (with one triple bond)

- linear geometry at C≡C carbons
- *sp* hybridization at C≡C carbons
- no "*cis - trans*" isomers
- similar addition reactions as alkenes
  (stepwise addition can occur)



(d) Aromatic Hydrocarbons (Benzene and it's derivatives)

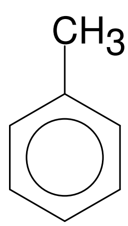
Benzene ~ C_6H_6



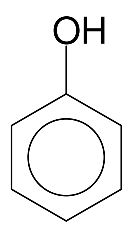
- planar 6-membered ring (especially stable)
- all C-C distances equivalent
- *sp^2* hybridization at all carbons
- *delocalized* set of 3 double bonds (6 π electrons)

Derivatives of Benzene

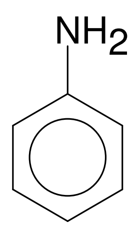
- common names ~ monosubstituted



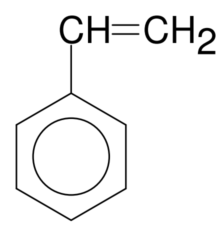
toluene



phenol

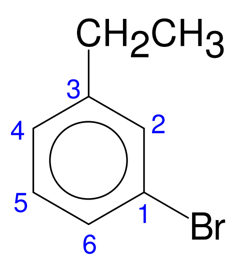


aniline

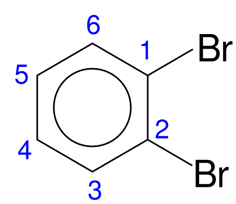


styrene

- systematic names ~ disubstituted

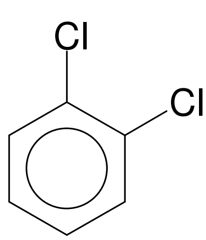


1-bromo-3-ethylbenzene

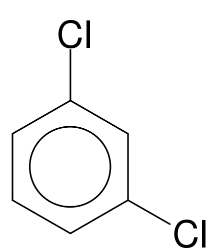


1,2-dibromobenzene

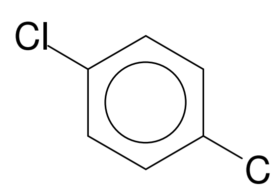
- *ortho, meta, para* designators



o-dichlorobenzene

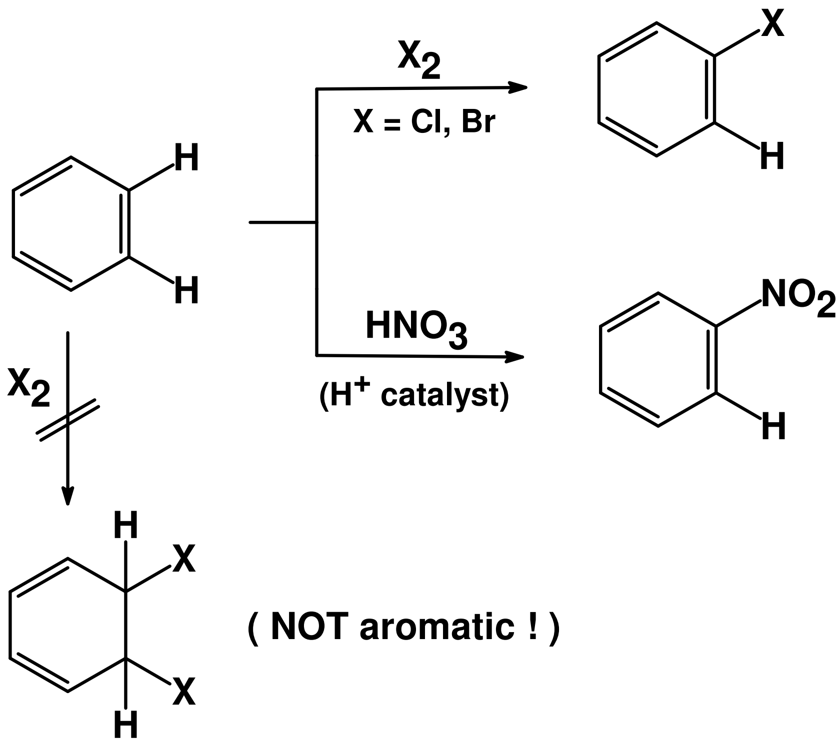


m-dichlorobenzene



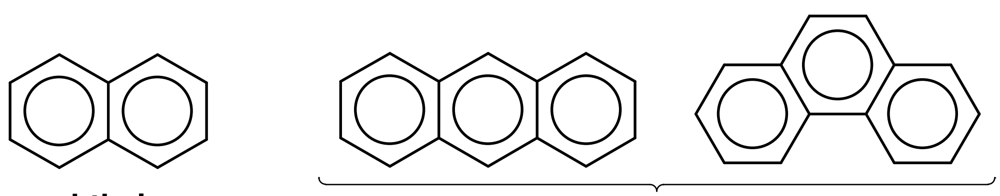
p-dichlorobenzene

Substitution Reactions (never addition!)



(NOT aromatic !)

other common aromatic hydrocarbons:



naphthalene

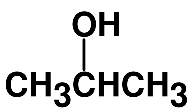
anthracenes

(4) Alcohols and Ethers (organic derivatives of H_2O)

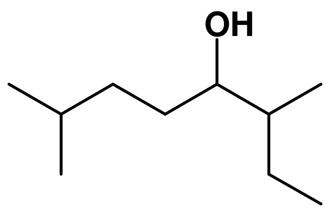
Nomenclature

***Alcohols*, R-O-H**

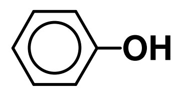
R =	CH_3	methanol
R =	CH_3CH_2	ethanol
R =	$CH_3CH_2CH_2$	1-propanol (*n*-propanol)



2-propanol
(*iso*-propanol)



3,7-dimethyl-4-octanol

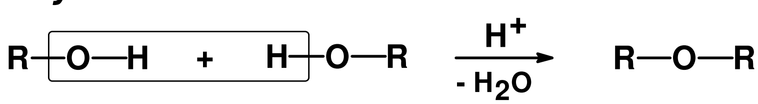


phenol

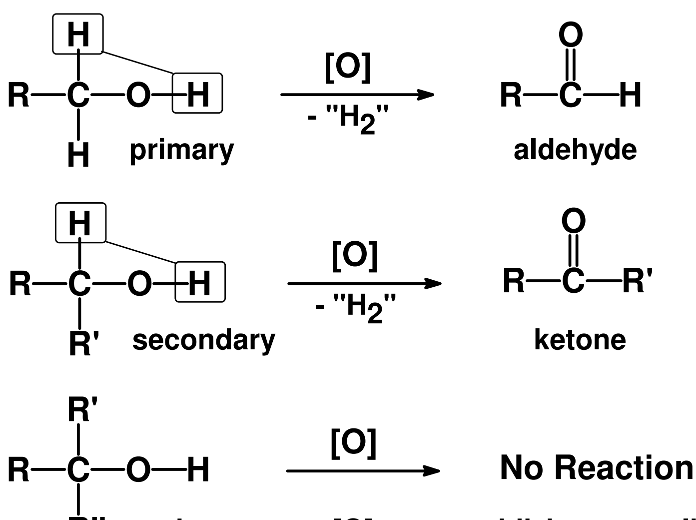
***Ethers*, R-O-R'**

CH_3CH_2-O-CH_2CH_3	diethyl ether
CH_3-O-$CH_2CH_2CH_3$	methyl propyl ether

Ether *Synthesis*:

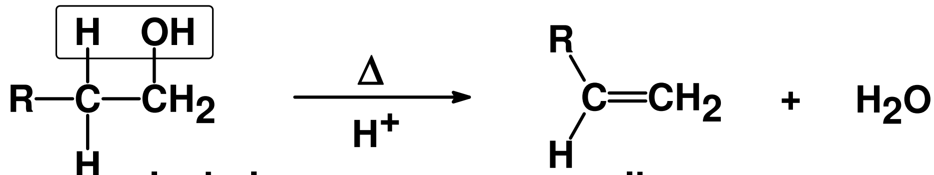


Oxidation of alcohols



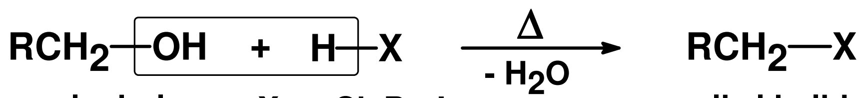
[O] = an oxidizing agent like $[Cr_2O_7]^{2-}$

Elimination Reactions of alcohols



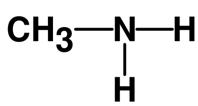
alcohol alkene

Substitution Reactions of alcohols

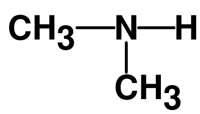


alcohol X = Cl, Br, I alkyl halide

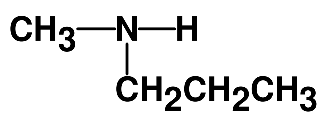
(5) Amines (organic derivatives of NH_3)



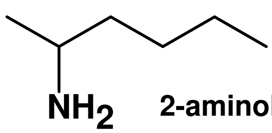
methylamine



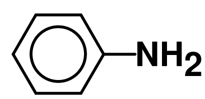
dimethylamine



methylpropylamine



2-aminohexane



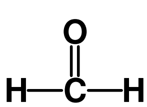
aniline

like ammonia, **amines are *weak bases***

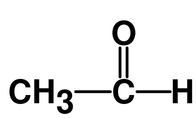
$$RNH_2 + H^+ \rightleftharpoons RNH_3^+$$

(6) Aldehydes and Ketones

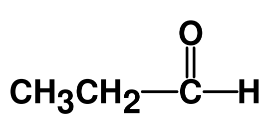
Nomenclature



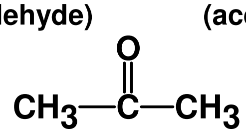
methanal
(formaldehyde)



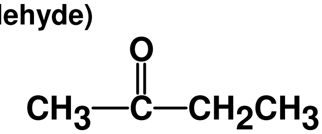
ethanal
(acetaldehyde)



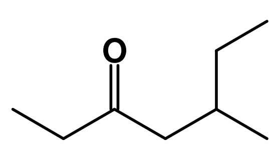
propanal



propanone
(acetone)

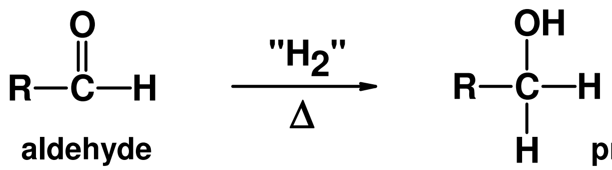


butanone
(methyl ethyl ketone)

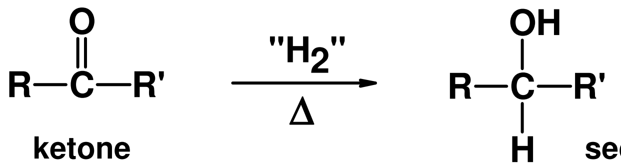


5-methyl-3-heptanone

Hydrogenation (reduction) of aldehydes and ketones

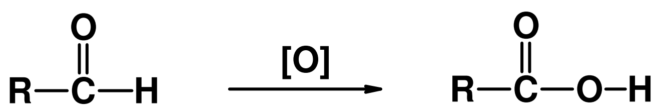


aldehyde → primary alcohol



ketone → secondary alcohol

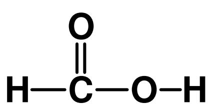
Oxidation of aldehydes (very easy!)



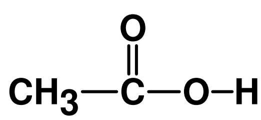
aldehyde → carboxylic acid

(7) Carboxylic Acids and Esters

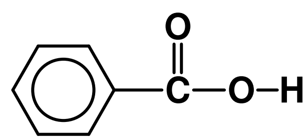
Nomenclature of Acids



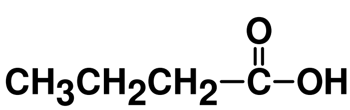
methanoic acid
(formic acid)



ethanoic acid
(acetic acid)



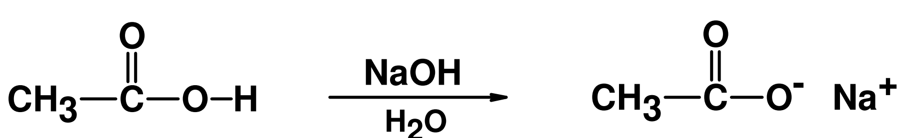
benzoic acid



butanoic acid

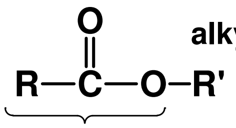
≡ $CH_3CH_2CH_2CO_2H$
(condensed formula)

Salts of Acids



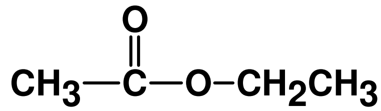
acetic acid → sodium acetate

Nomenclature of Esters

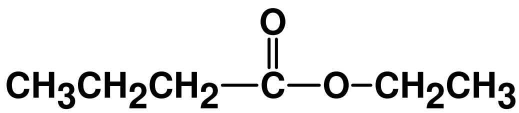


alkyl group

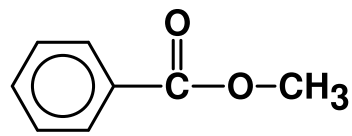
acid name
-ate



ethyl acetate

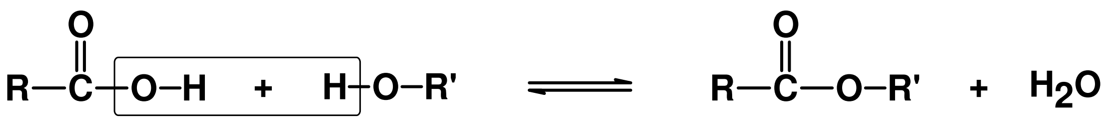


ethyl butanoate

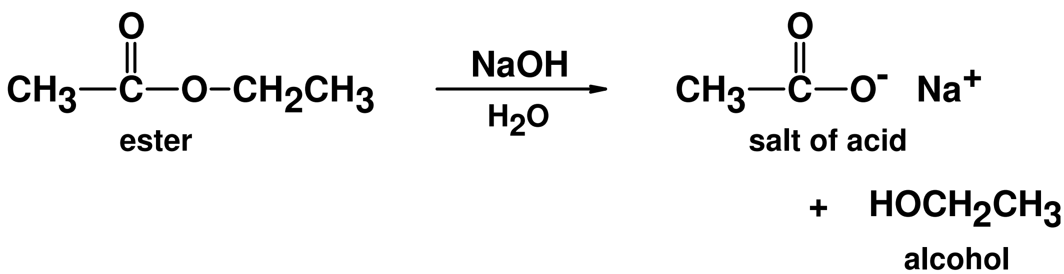


methyl benzoate

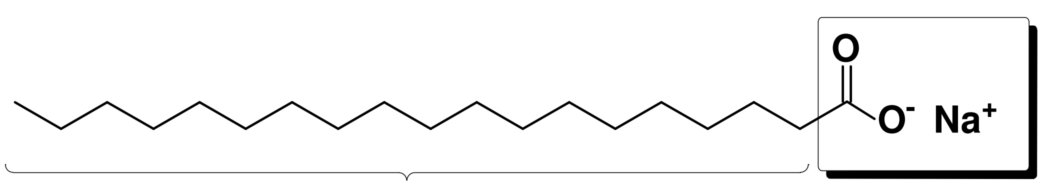
Formation of Esters (from acid + alcohol)



Saponification of Esters (hydrolysis)



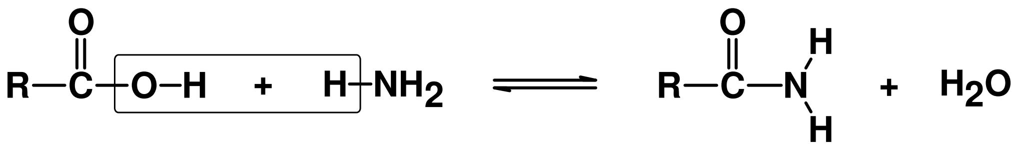
Soap ~ salt of long chain carboxylic acid



non-polar hydrocarbon "tail" polar "head"

(8) Amides

acid derivatives (e.g., 1° amides: $-NH_2$ instead of -OH)



Nomenclature

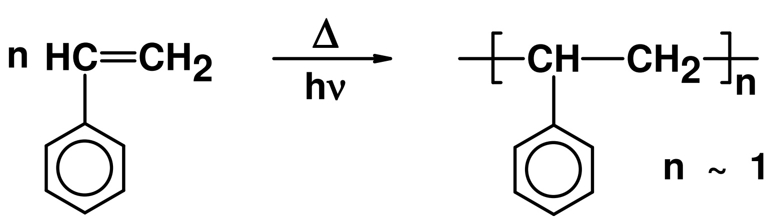
R = CH_3	ethanamide
R = $CH_2CH_2CH_2CH_3$	pentanamide, etc.

amides **(unlike amines) are generally *not basic***
(due to e^- withdrawing effect of the C=O group)

Organic Polymers (Section 12.9)

(1) Polymers -- *macromolecules* made up of many repeating units called *monomers*

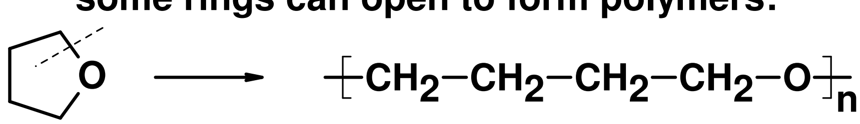
e.g., *poly*styrene is formed via the *polymerization* of the monomer, styrene:



n ~ 10^3 - 10^6

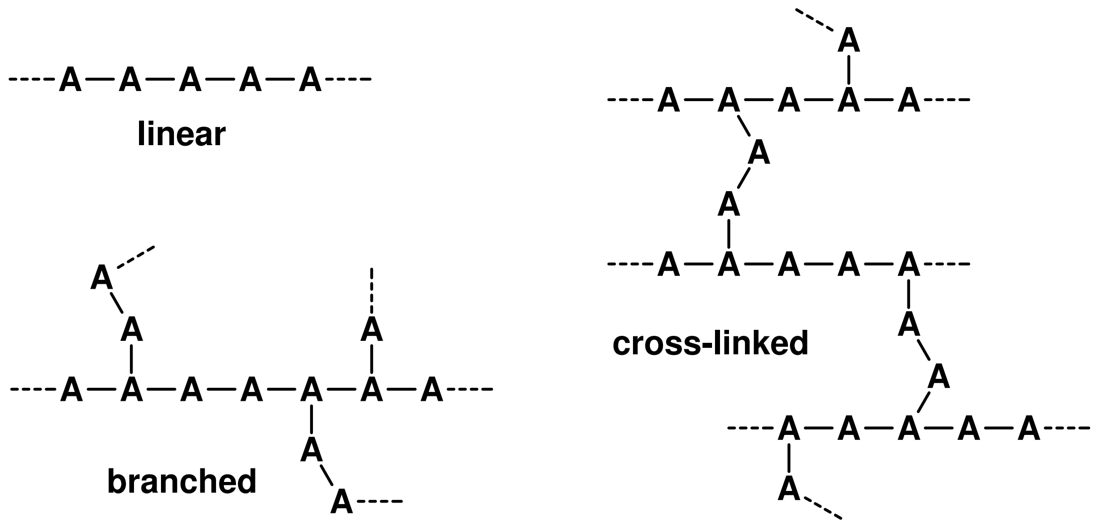
styrene **polystyrene**

e.g., some rings can open to form polymers:



(2) Types of polymer structures

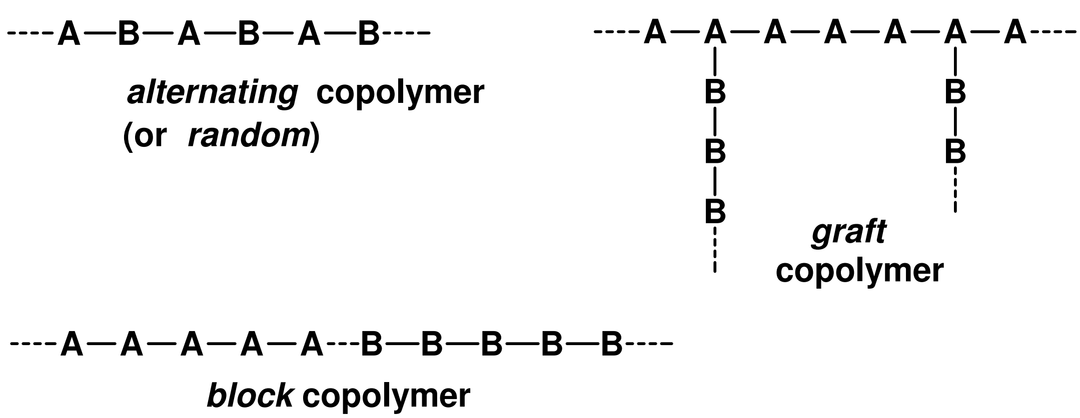
*Homo*polymers



Solubility linear and branched -- usually soluble
cross-linked -- insoluble (swell)

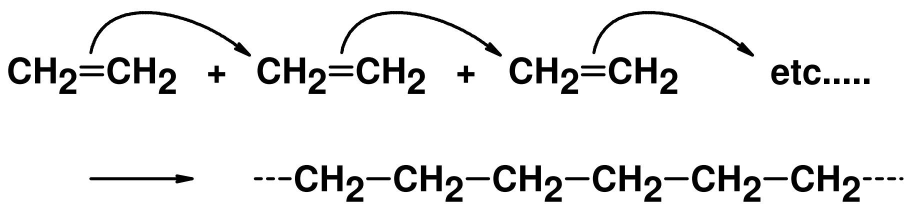
Elastomer a lightly cross-linked polymer

***Co*polymers** -- contain two or more different monomers, combine properties of 2 polymers



(3) Methods of Polymerization

Addition **(very common -- works with most alkenes)**



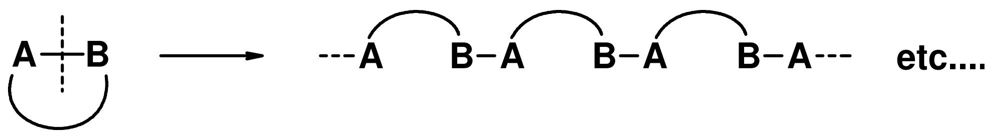
requires an *initiator* (e.g., a catalyst or UV light) to start the "chain" reaction

Condensation **(common for polyesters and polyamides)**

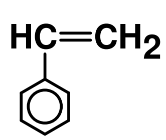
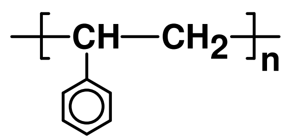
a small molecule (e.g., H_2O) byproduct is formed

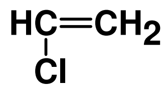
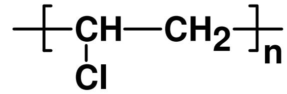
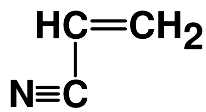
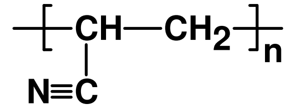
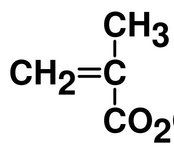
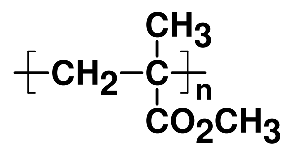
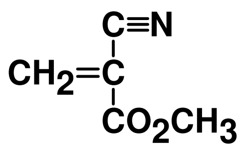
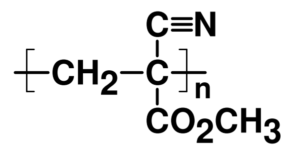
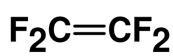
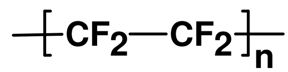
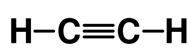
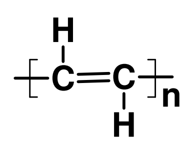
$$X{-}A{-}Y \;+\; X{-}B{-}Y \xrightarrow{-\,XY} \left[A{-}B \right]_n$$

Ring-Opening **(uncommon except for polyethers and most inorganic polymers, e.g., silicones)**

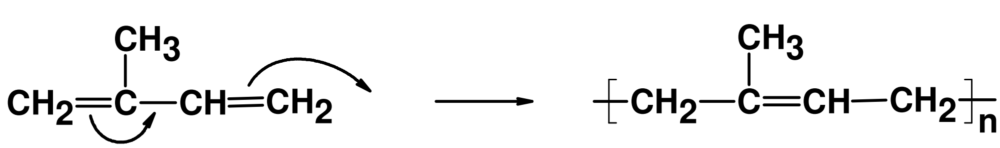


(4) Common Addition Polymers

Monomer	Polymer
$CH_2{=}CH_2$ ethylene	$\left[CH_2{-}CH_2 \right]_n$ polyethylene
 styrene	 polystyrene

 vinyl chloride	 poly(vinyl chloride) ~ PVC
 cyanoethene	 "Orlon"
 (ester) methyl methacrylate	 "plexiglas" (Lucite)
 methyl cyanoacrylate	 "super glue"
 tetrafluoroethene	 "Teflon"
 acetylene (ethyne)	 poly(acetylene)

Addition polymerization of *dienes*

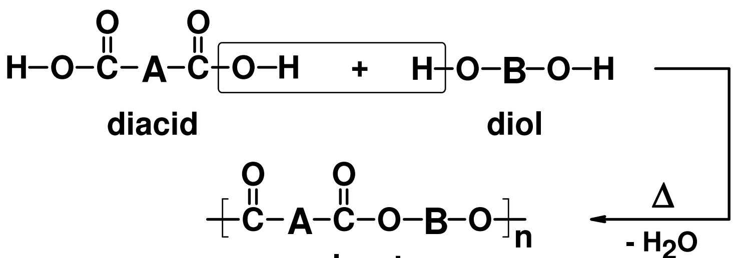


"isoprene"
(2-methyl-1,3-butadiene)

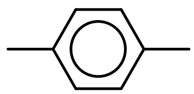
"natural" rubber

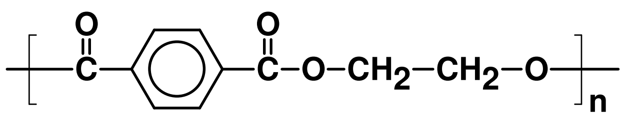
(5) Common Condensation Polymers

Polyesters



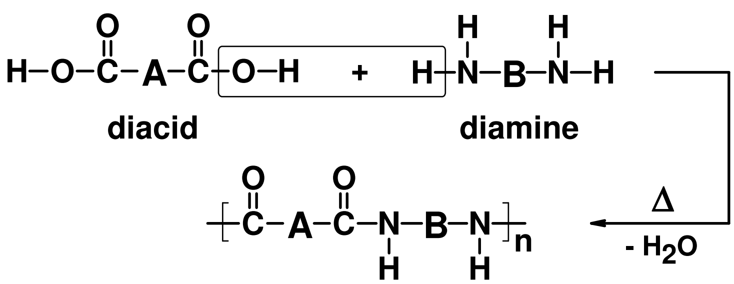
polyester

e.g., A =  B = —CH_2—CH_2—



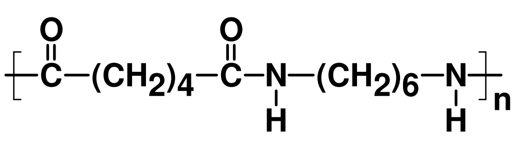
"Dacron"

Polyamides (nylons)

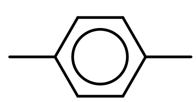


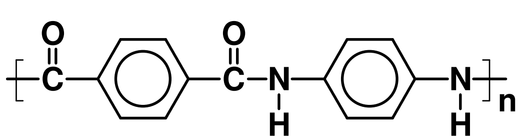
polyamide

e.g., A = —$(CH_2)_4$— B = —$(CH_2)_6$—



nylon-66

e.g., A = B = 



"Kevlar"