



TOPIC 8:

Reactions in Organic Chemistry

Alkanes

Cycloalkanes

Alkenes

Alkynes

Aromatic hydrocarbons

Alcohols and phenols

Ethers

Thiols

Carbonyl compounds

Carboxylic compounds

Derivatives of carboxylic acids

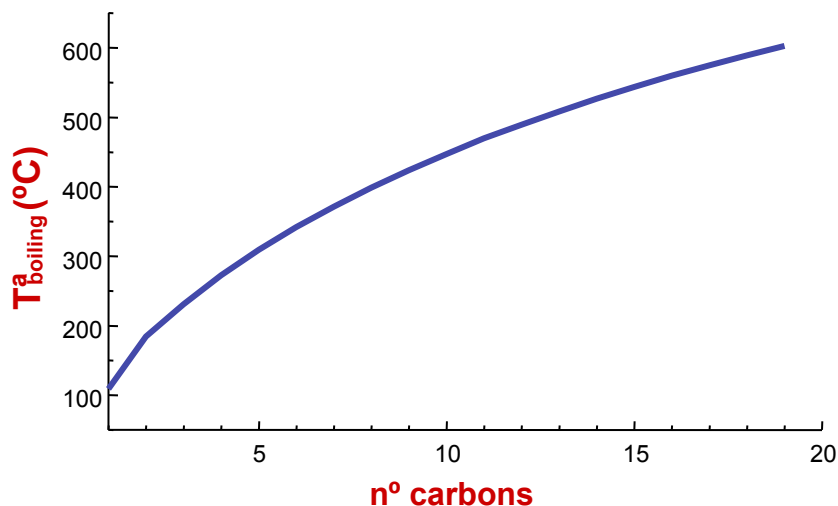
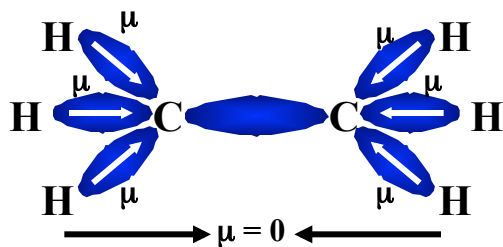
Amines



Alkanes ($\text{—CH}_2\text{—}$)

Saturated hydrocarbons, aliphatic or paraffins


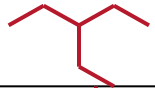
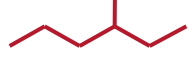

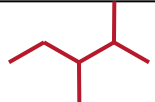



Almost all are obtained from petroleum



The strength of London forces increases with molar mass. Branching decreases molecular packing, increases intermolecular distance and decreases London forces

$$\Delta H_{\text{dis}} (\text{C-C}) = 347 \text{ KJ}\cdot\text{mol}^{-1}$$

$$\Delta H_{\text{dis}} (\text{C-H}) = 415 \text{ KJ}\cdot\text{mol}^{-1}$$

COMPOUND	T _b
 heptane	98,4
 3-ethyl pentane	93,5
 3-methyl hexane	92,0
 2-methyl hexane	90,0
 2,3-dimethyl pentane	89,8
 3,3-dimethyl pentane	86,1
 2,4-dimethyl pentane	80,5
 2,2-dimethyl pentane	79,2

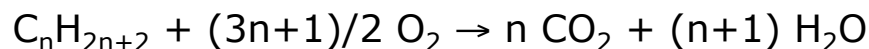


Reactivity

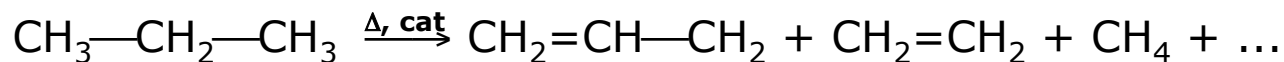
All electron pairs shared in σ bonds. Very low reactivity

Only substitution and elimination reactions

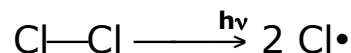
Combustion



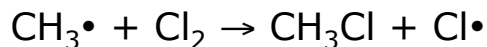
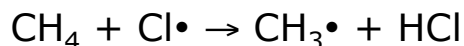
Cracking



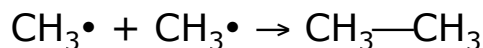
Halogenation



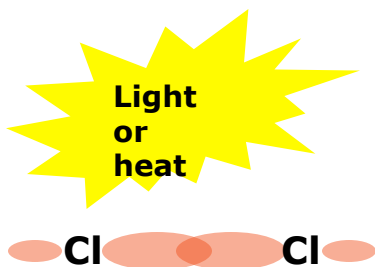
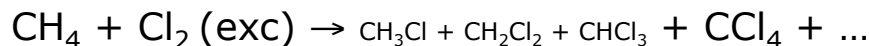
Initiation



Propagation



Termination

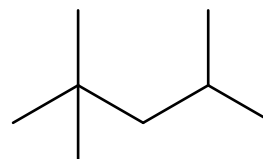




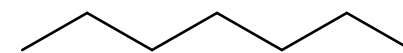
Octane rating

- Octane rating is a measure for the quality of gasoline as a fuel for internal combustion engines.
- Fuels have tendency to self ignite during compression prior to the desired position of the piston in the cylinder as appropriate for valve and ignition timing: the consequence is Engine Knocking, a characteristic metallic "pinging" sound that damages the engine.

- Two hydrocarbons are the references: heptane (octane rating 0) and 2,2,4-trimethylpentane (octane rating 100)



Iso-octane

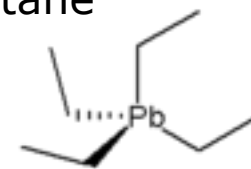


Heptane

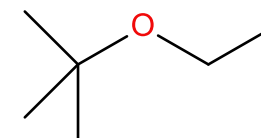
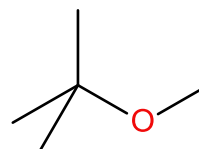
- A fuel with 90 octane rating means that it has the same anti-knocking properties as a mixture of 90% iso-octane and 10 % heptane.

- There are fuels with better octane rating than 100: 2,2,3-trimethylpentane (106), methanol and ethanol (☒109).

- Tetraethyl lead was used in the past as an octane booster
- Other additives are used nowadays: methyl-*tert*-butyl ether (MTBE) and ethyl-*tert*-butyl ether(ETBE)



Who is who?

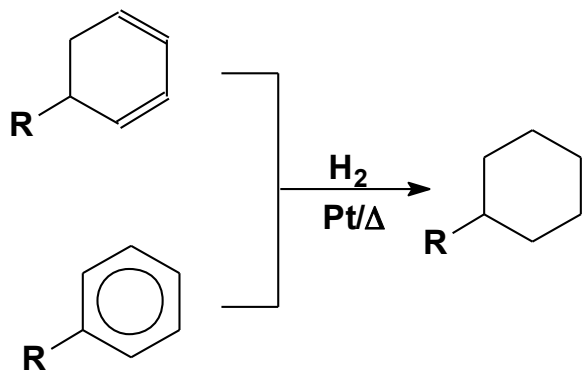




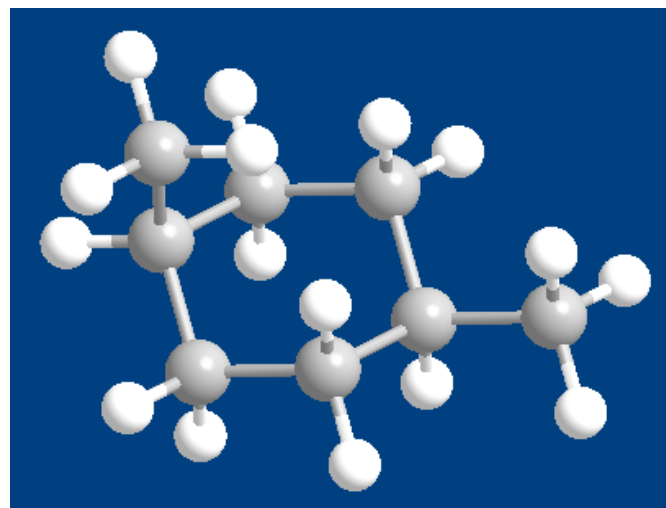
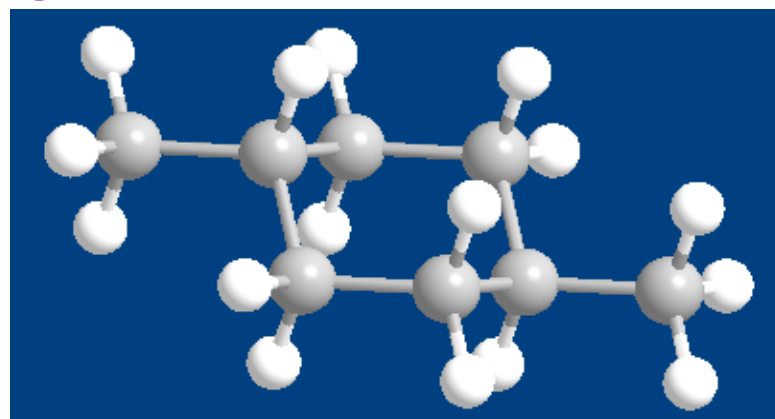
Cycloalkanes (CH_2)

Similar properties to alkanes

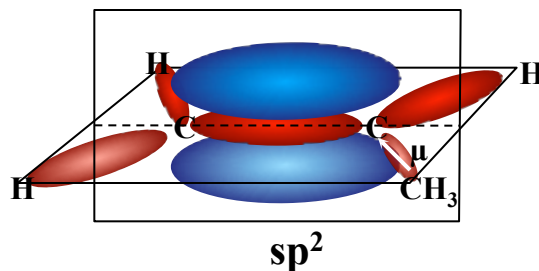
Synthesis: Addition. Catalytic hydrogenation



*Two isomers of
1,4-dimethylcyclohexane.
Are they different? How can we name
them*



Alkenes (—CH=CH—)

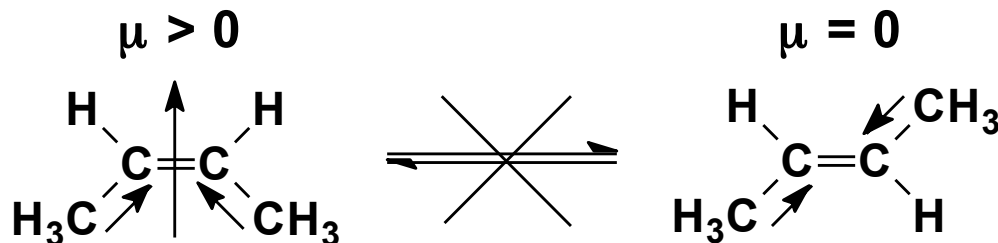


$$\Delta H_{\text{dis}} (\text{C}=\text{C}) = 610 \text{ KJ}\cdot\text{mol}^{-1}$$

$$\chi_{\text{C}_{sp^3}} < \chi_{\text{C}_{sp^2}}$$

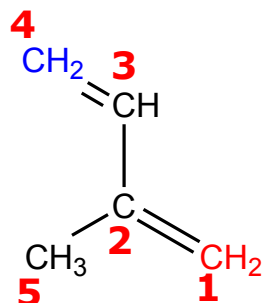
- Double bonds.
- High electron density. **Electron deficient reactants will attack =**
- Nucleophilic reactive. **= will attack nucleophilic centers**
- Similar physical properties than alkanes
- Almost all from petroleum

● Cis-trans isomers



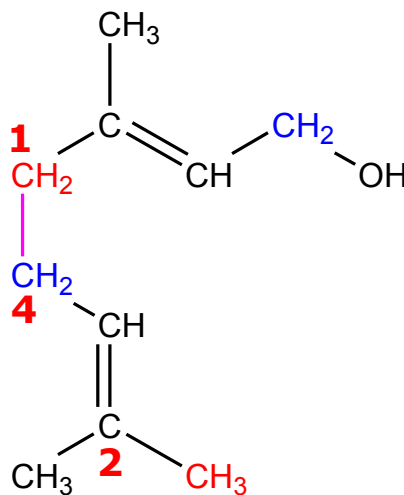
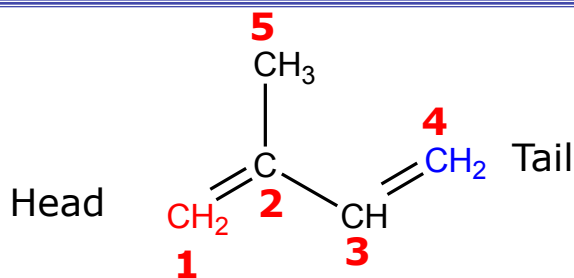
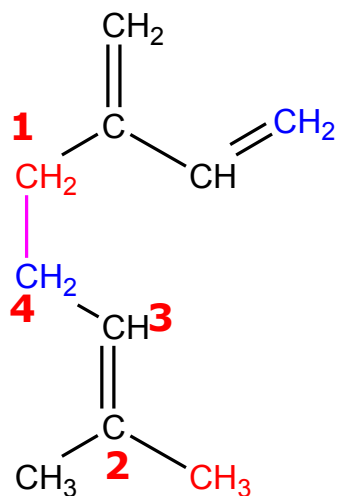


Terpenes



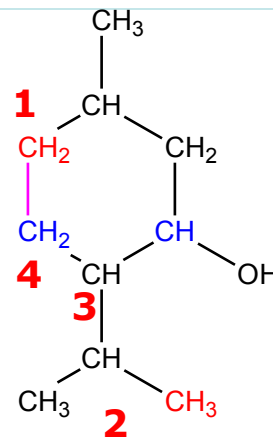
Isoprene

2 basic units of isoprene
Head-to Tail
Myrcene (bay oil-laurel)

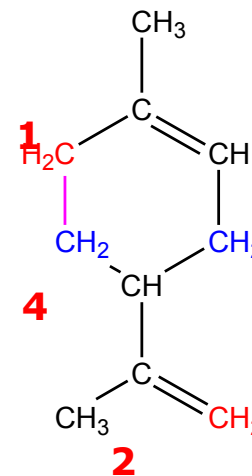


2 basic units of isoprene
Head-to Tail plus an
additional OH
Geraniol (Rose)

2 basic units of isoprene
Head-to Tail plus an additional
closing bond and OH
Menthol

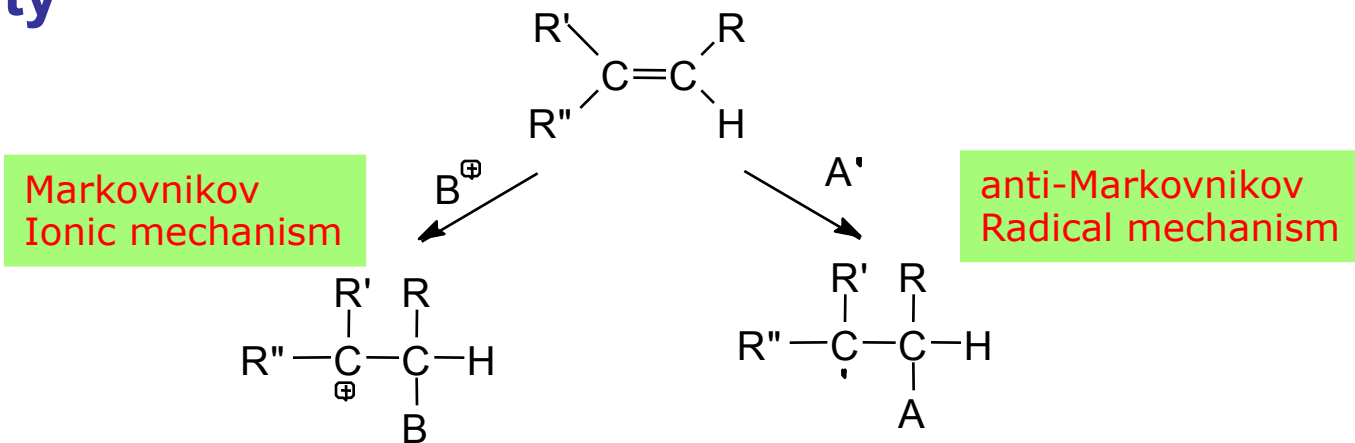


Basic unit isoprene: 2-Methyl-1,3-butadiene



2 basic units of isoprene
Head-to Tail plus an additional
closing bond
Limonene

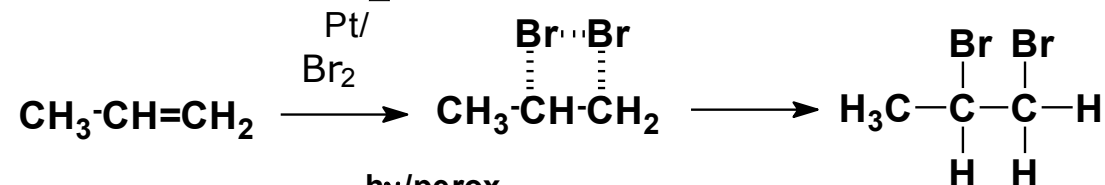
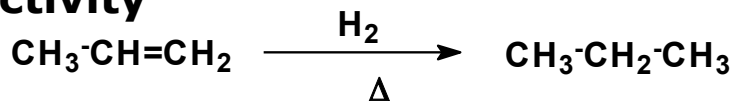
Reactivity



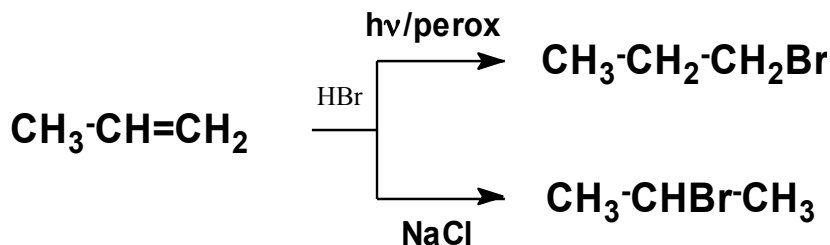
➤ Addition reactions: Regioselectivity

Catalytic hydrogenation

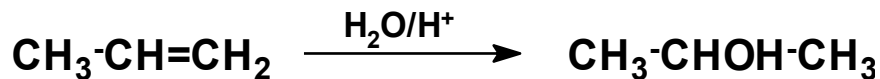
Halogenation



Hydrohalogenation

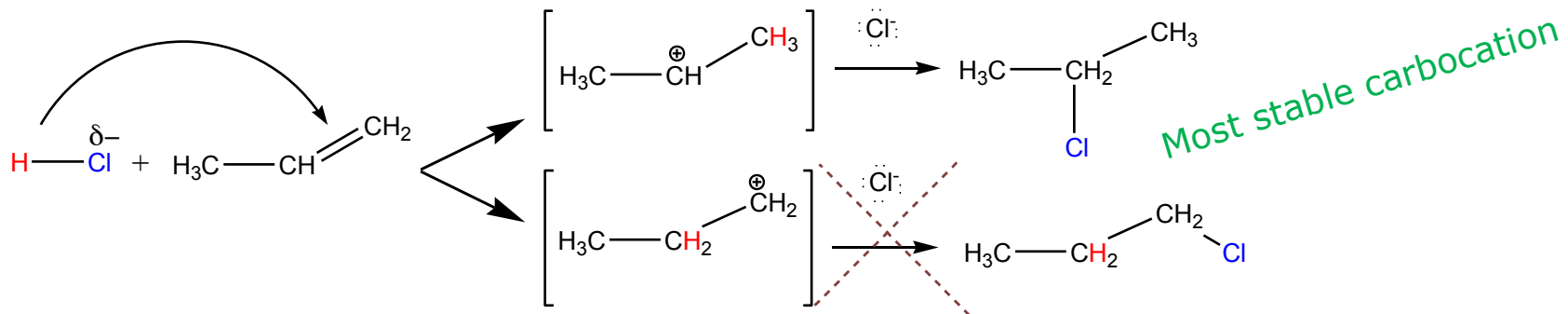


Water in acid media

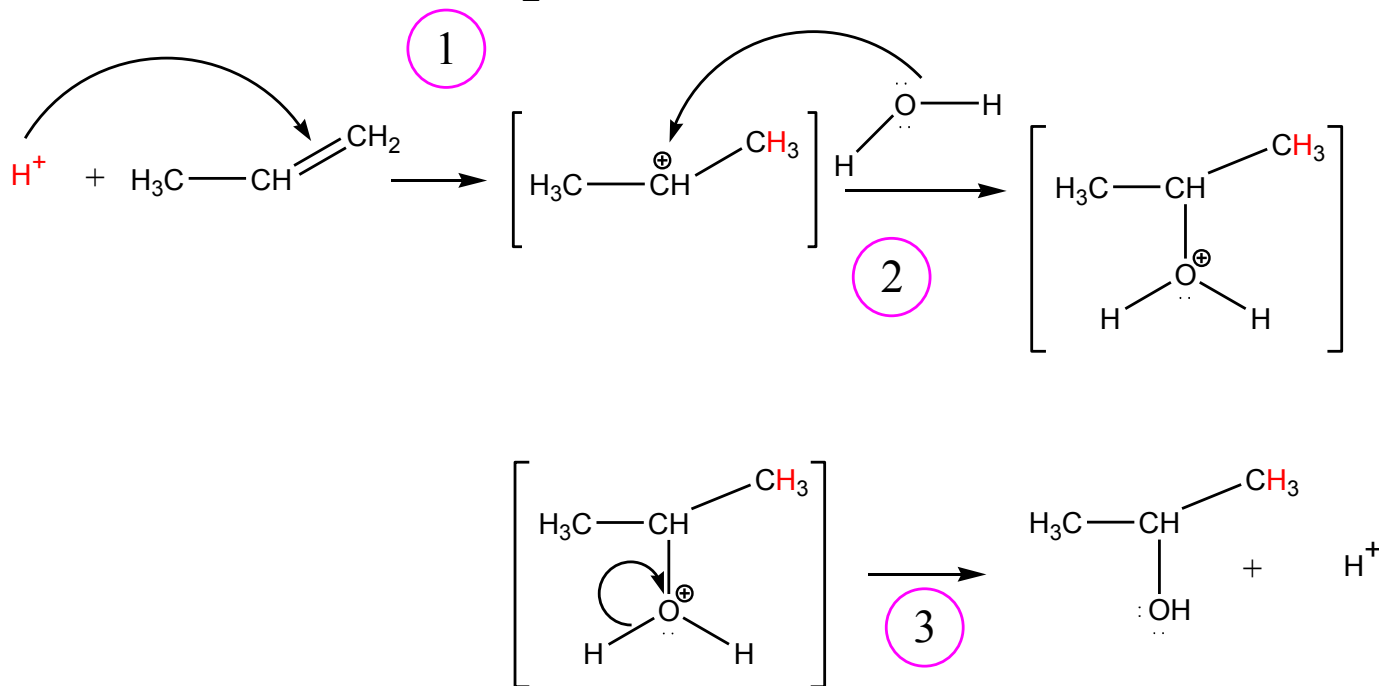




Mechanism of Markovnikov HCl addition



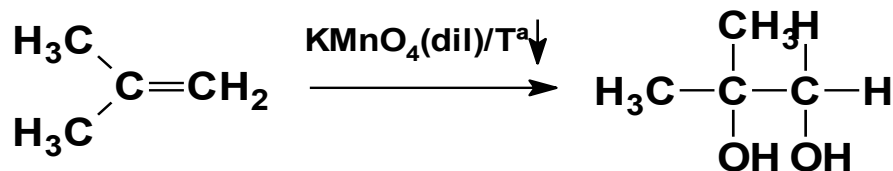
Mechanism of Markovnikov H_2O addition in acidic media



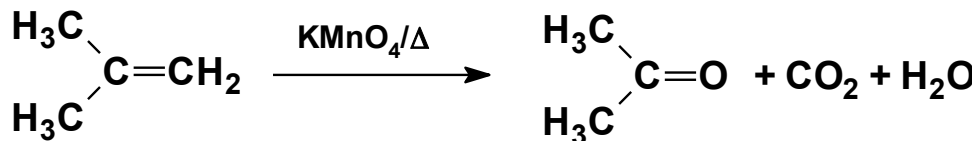


Oxidation

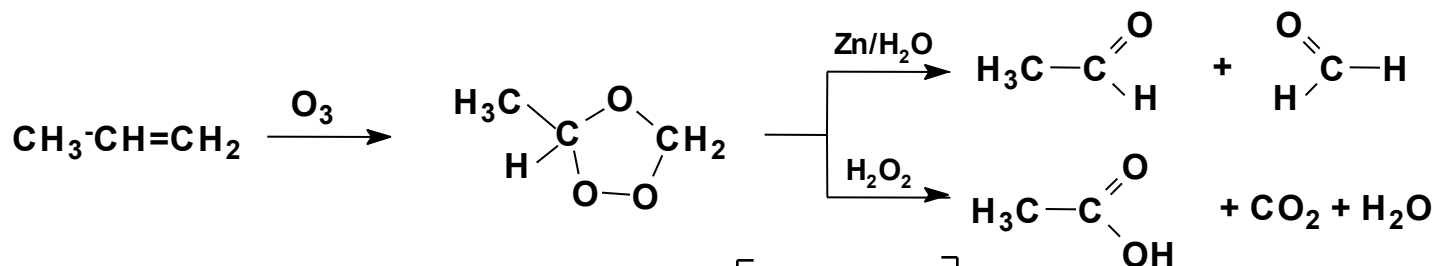
Mild



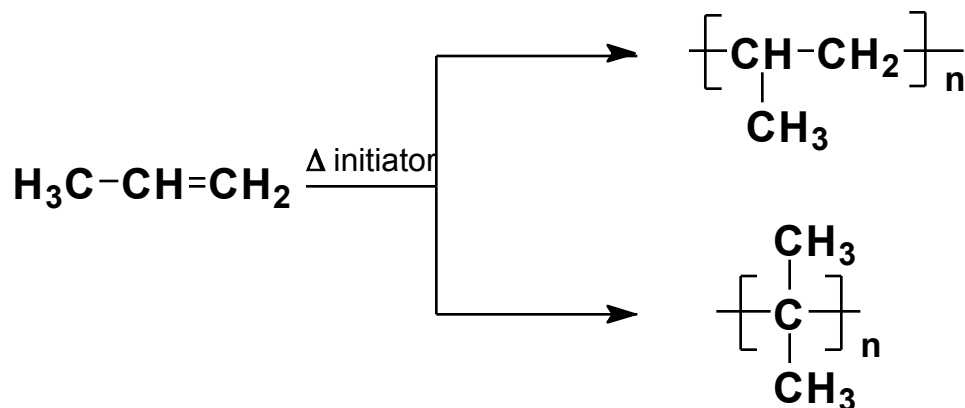
Strong



Ozonolysis

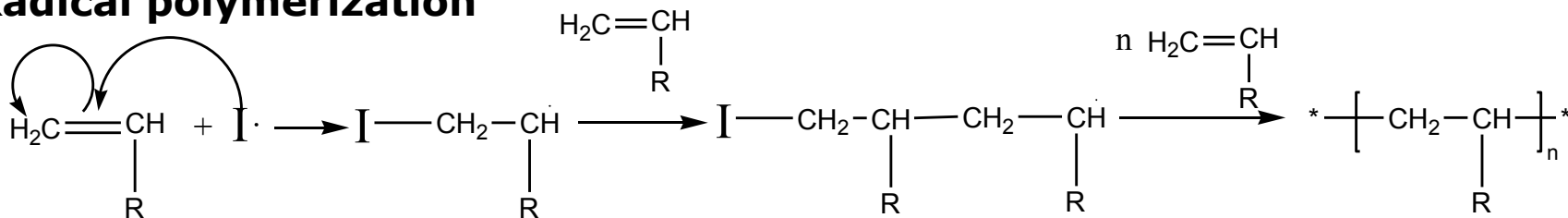


Polymerization

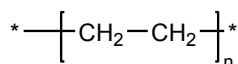
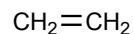




Radical polymerization

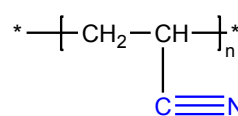
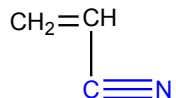


Ethylene



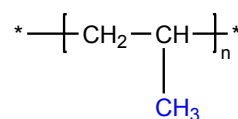
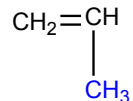
Polyethylene

Acrylonitrile



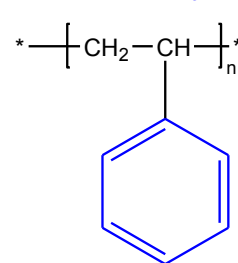
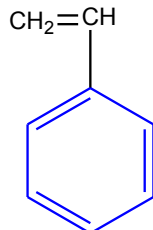
Polyacrylonitrile

Propylene



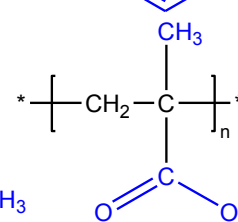
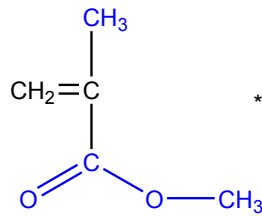
Polypropylene

Styrene



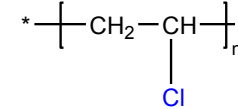
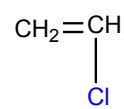
Polystyrene

Methylmetacrylate

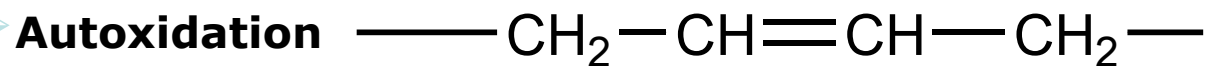


Polymethylmetacrylate

Vinyl chloride



Poly(vinyl chloride)



1
Chain initiation



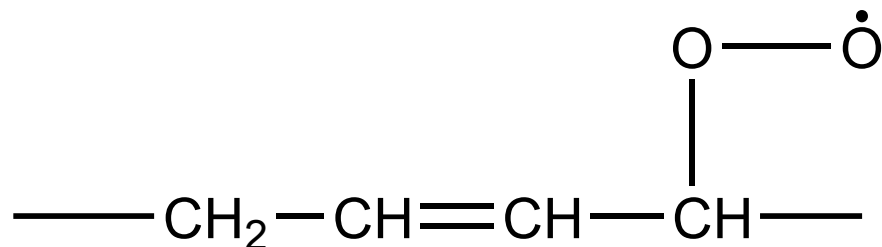
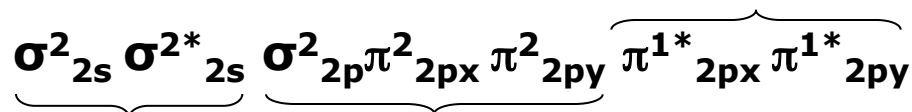
Light or heat



2a
Chain propagation



O₂ is a diradical:



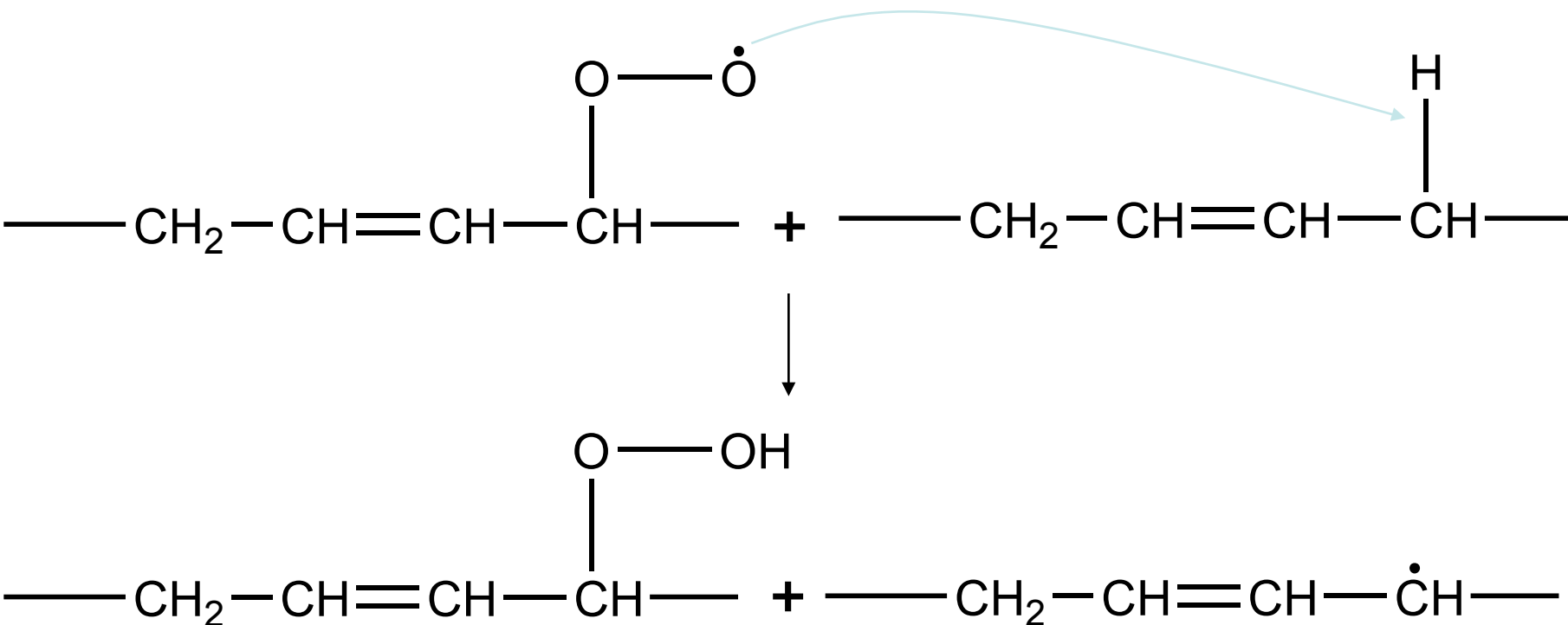
Hydroperoxide radical



Autoxidation

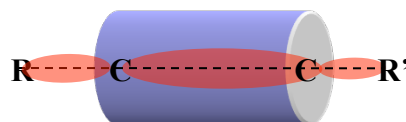
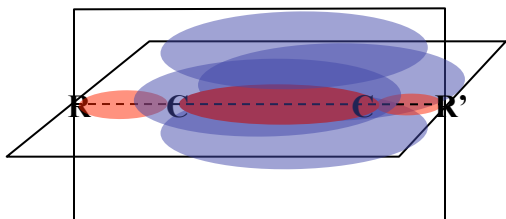
2b

Chain propagation



This process is responsible for the oxidation of unsaturated fatty acids (cooking at high temperatures)

Alkynes ($\text{—C}\equiv\text{C—}$)

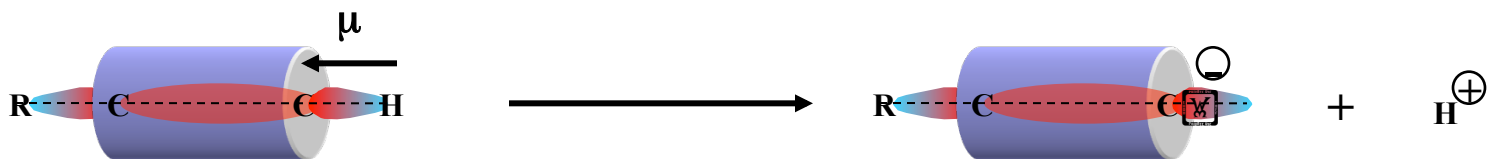


$$\Delta H_{\text{dis}} (\text{C}\equiv\text{C}) = 830 \text{ KJ}\cdot\text{mol}^{-1}$$

$$\chi_{\text{C}_{\text{sp}^2}} < \chi_{\text{C}_{\text{sp}}}$$

sp

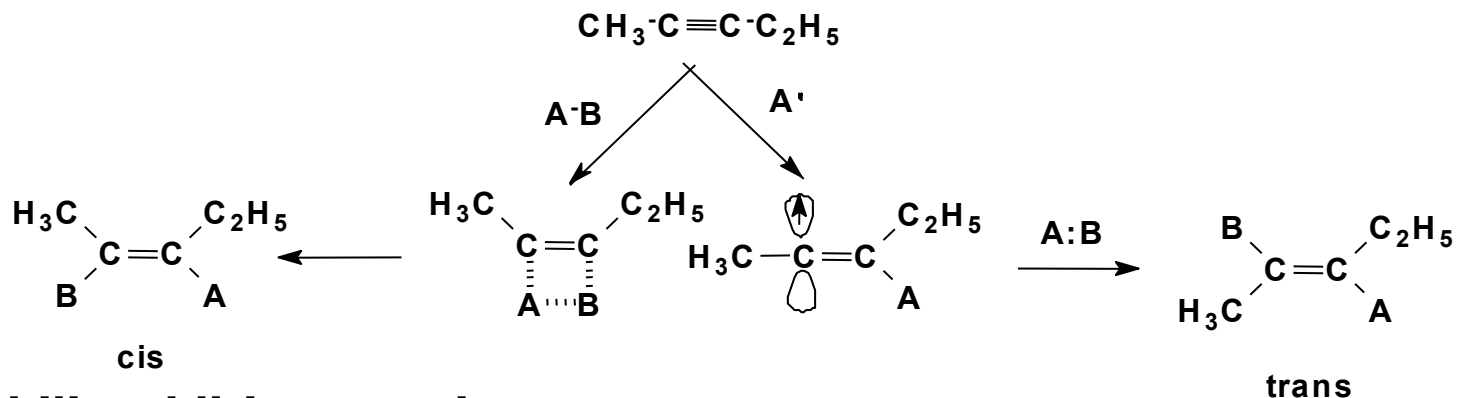
- Triple bond.
- High electron density.
- Nucleophilic reactive.
- Similar properties than alkenes



- Very weak acid properties. Only with very strong bases

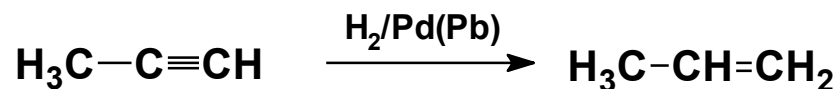


Reactivity

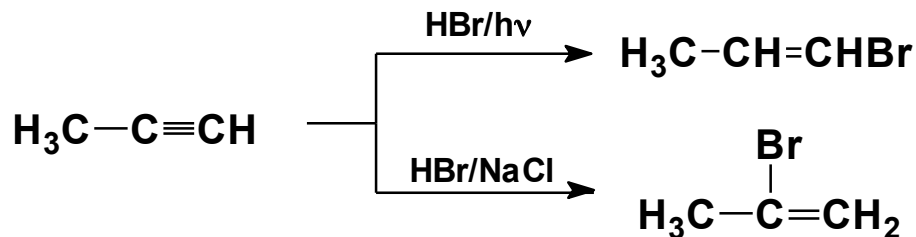


➤ Electrophilic addition reactions

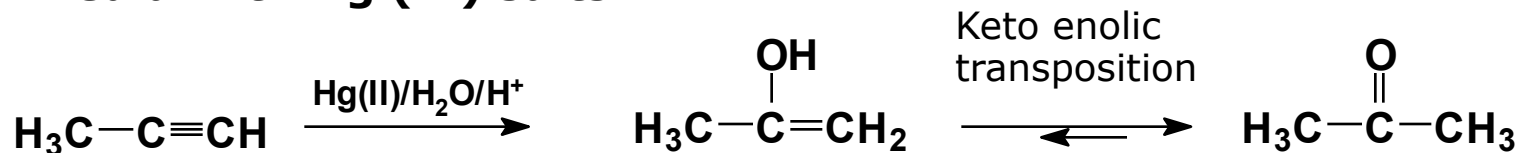
□ Catalytic hydrogenation



□ Hydrohalogenation

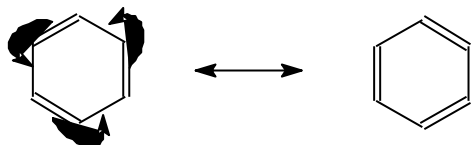


□ Water in acid media with Hg (II) salts



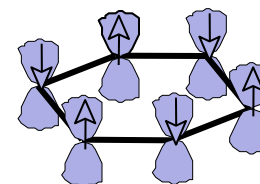
Aromatic hydrocarbons (\emptyset)

Reactivity



✓ $d(\text{C-C}) = \text{cte.}$ $d(\text{H-C}) = \text{cte.}$

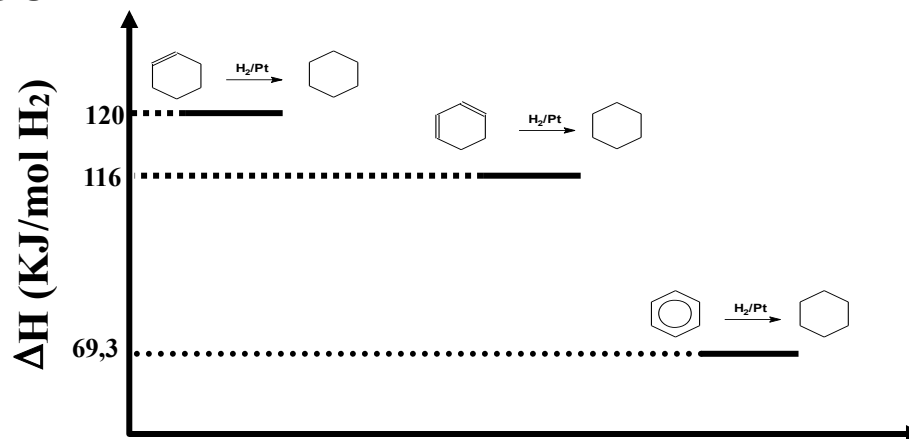
✓ $\widehat{\text{C-C-C}} = \text{cte.}$ $\widehat{\text{C-C-H}} = \text{cte.}$



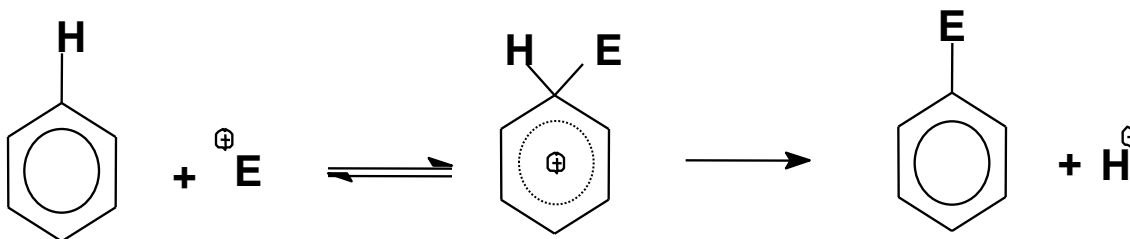
- Cyclic molecule
- Planar molecule
- $n^{\circ} e^{-} \pi = 4n + 2$

➤ Addition reactions

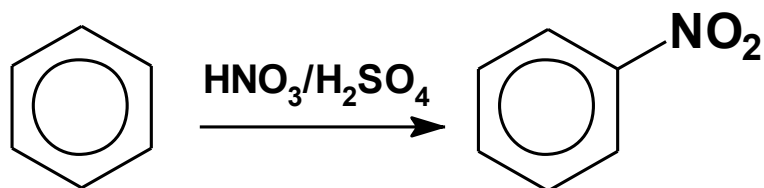
□ Catalytic hydrogenation



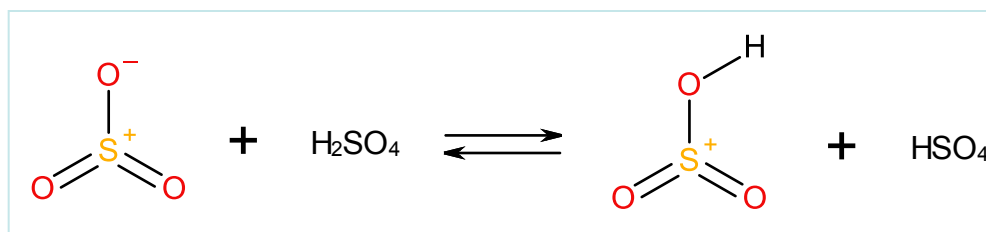
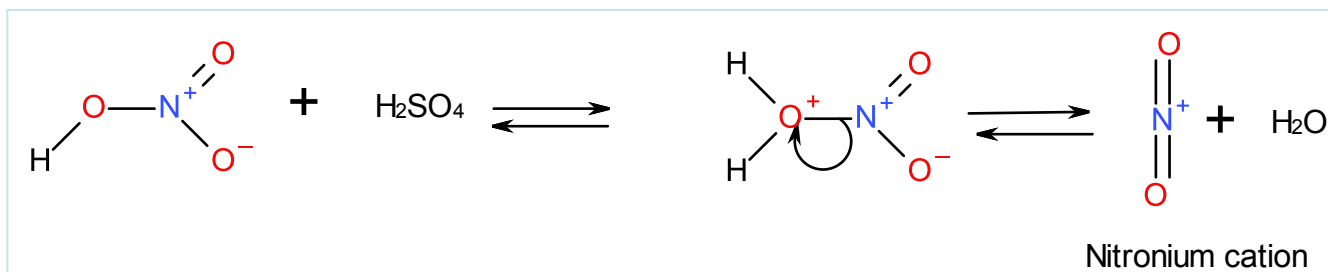
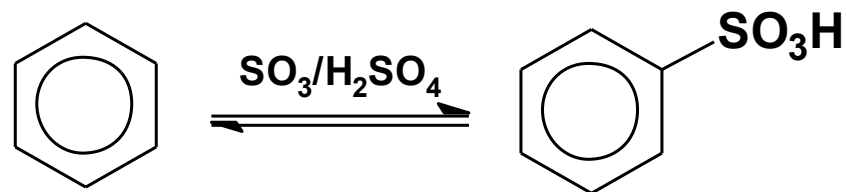
➤ Electrophilic substitution



▣ Nitration

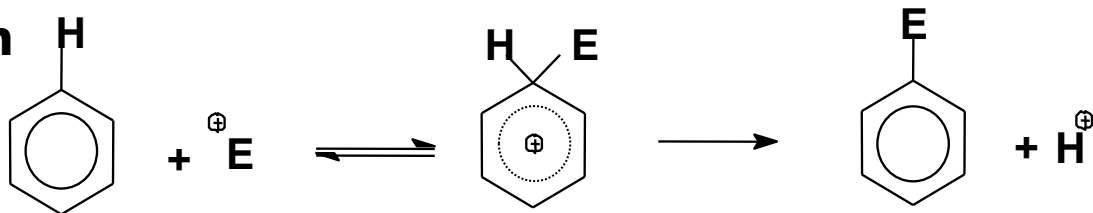


▣ Sulfonation

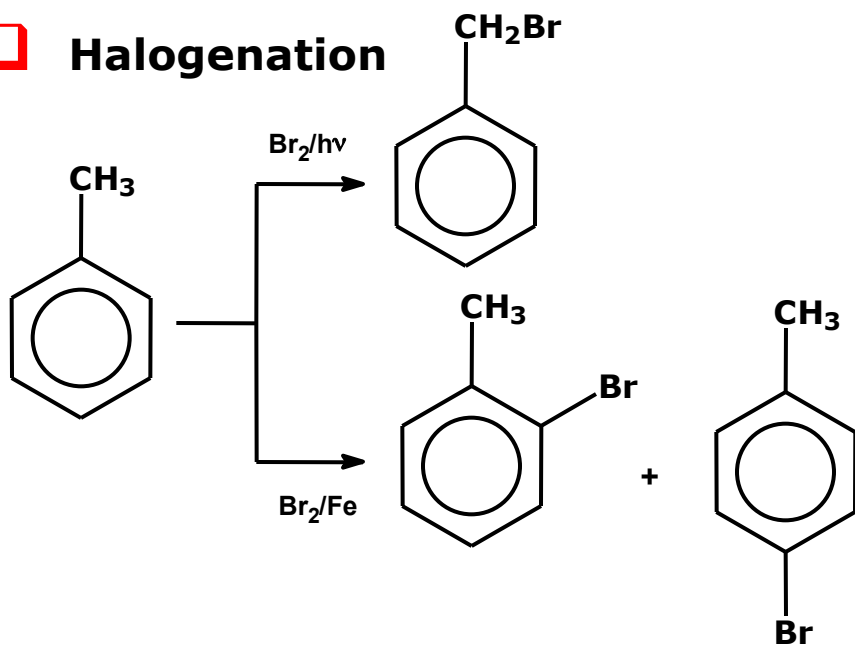




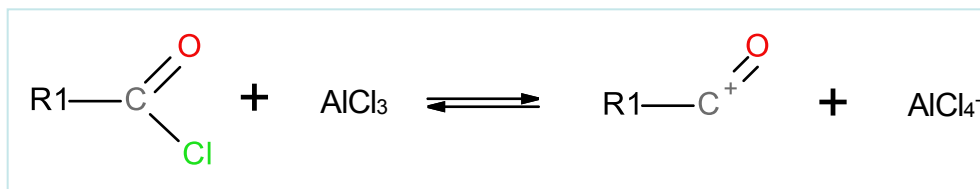
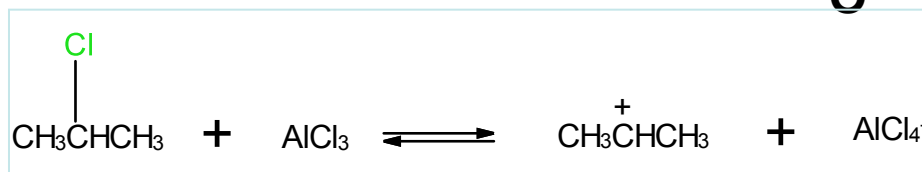
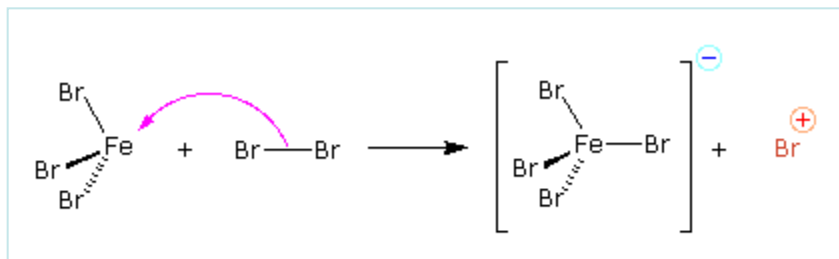
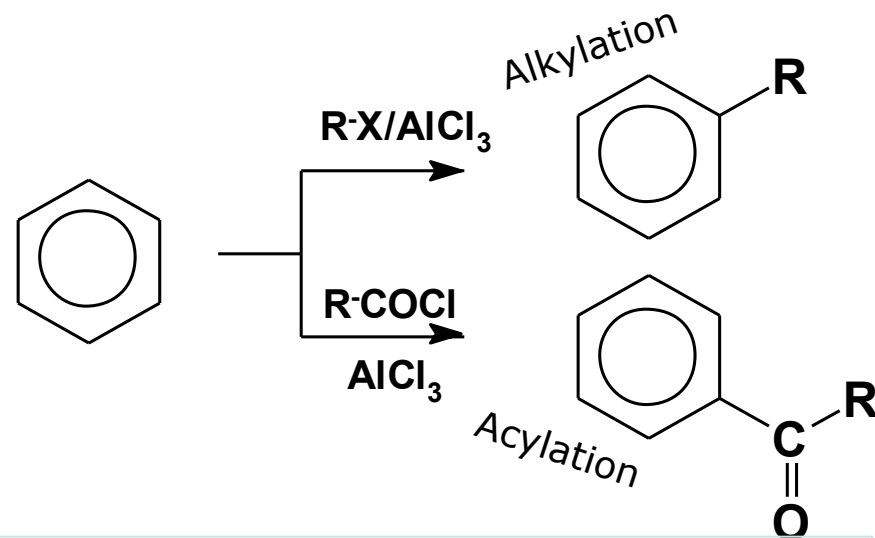
➤ Electrophilic substitution



□ Halogenation

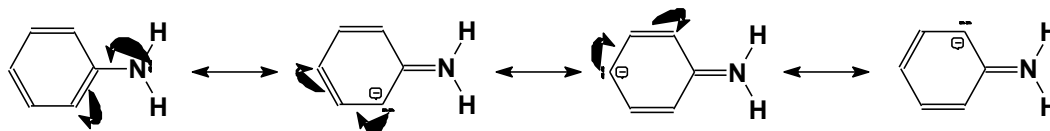


□ Friedel-Crafts



SUBSTITUTION ON BENZENE DERIVATIVES

Activating substituents (+R)

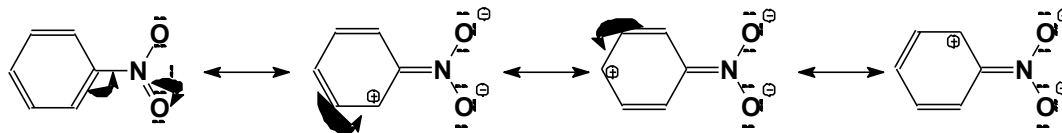


- ✓ Increased electron density
- ✓ Direct substitution to 2 and 4 (ortho and para) locations
- ✓ Higher reaction rates than benzene

-O⁻
-OH
-OR
-OC₆H₅
-OCOCH₃

-NH₂
-NR₂
-NHCOCH₃
-R₆
-C₆H₅

Deactivating groups (-R)



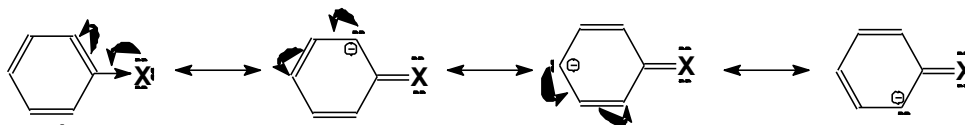
- ✓ Lower electron density
- ✓ Direct substitution to 3 (meta) location
- ✓ Lower reaction rates than benzene

-NO₂
-NR₃⁺
-PR₃⁺
-SR₂⁺
-SO₃H

-SO₂R
-CO₂H
-CO₂R
-CONH₂
-CHO

-COR
-CN

Strong deactivating groups directing ortho and para (+R, -I)



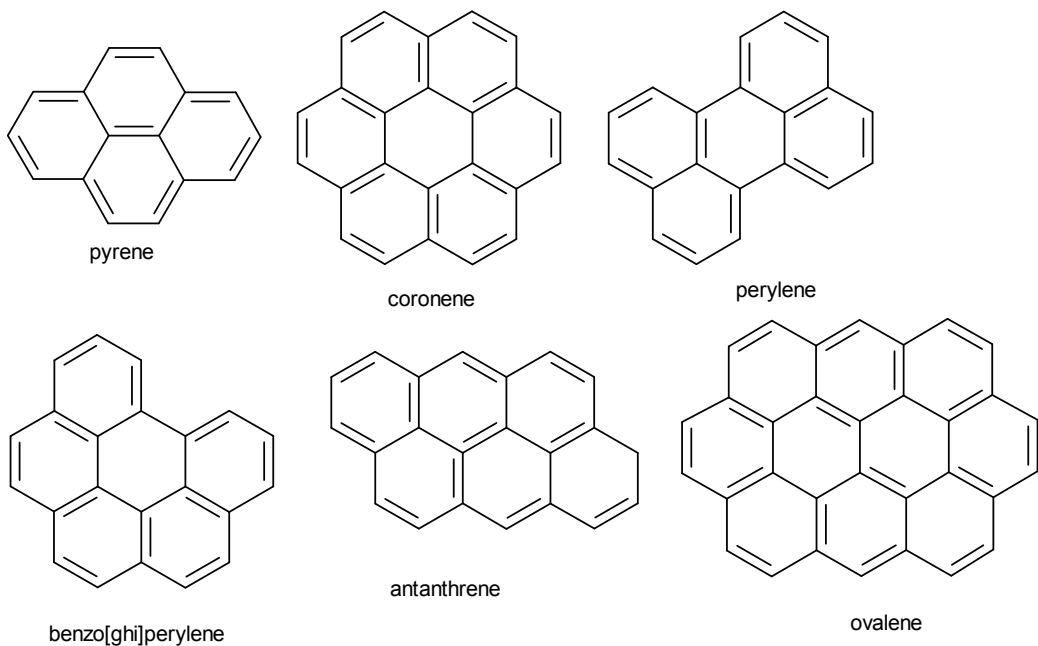
- ✓ Lower electron density
- ✓ Direct substitution to 2 and 4 (ortho and para) locations
- ✓ Lower reaction rates than benzene

-F
-Cl
-Br
-I
-CH₂Cl
-CH=CHNO₂

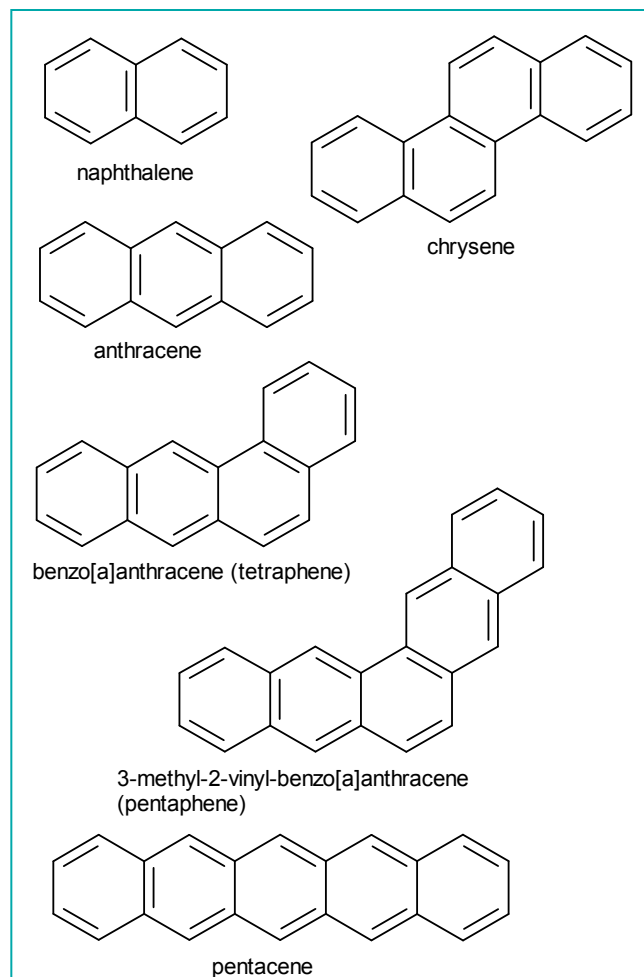


Polynuclear aromatic hydrocarbons

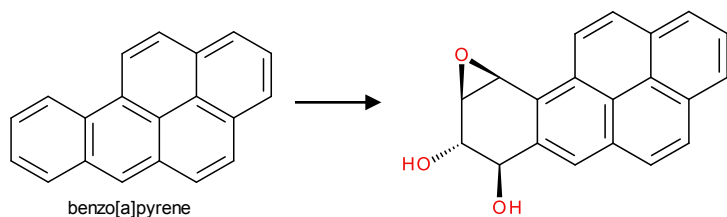
Pericondensed



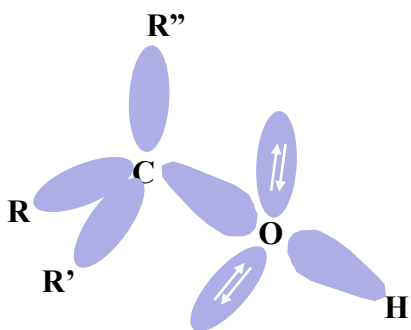
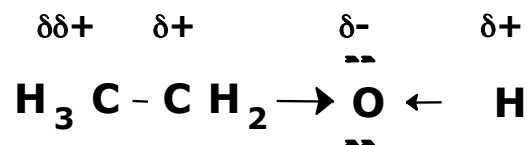
Catacondensed



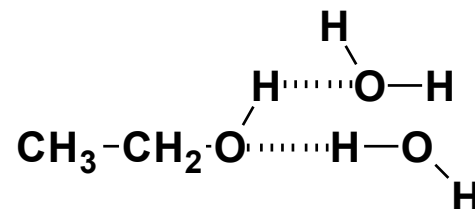
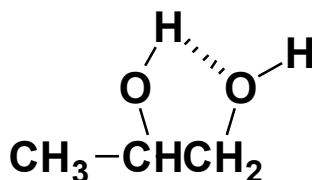
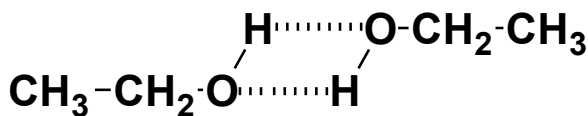
Benzo[a]pyrene is one of the most carcinogenic PAH's. It is enzymatically transformed by the organism into a more soluble form (epoxide and -OH) that can bind with DNA via some amino groups inducing mutations.



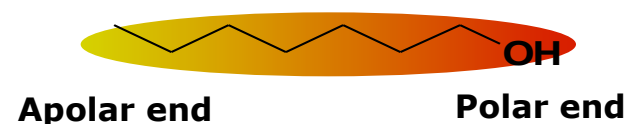
Alcohols and phenols (-OH)



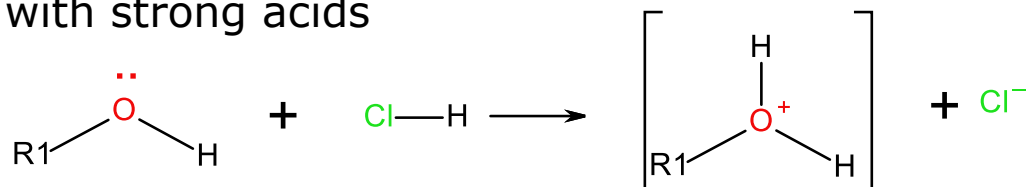
- Two free electron pairs → weak basic character
 - ✓ Nucleophilic reactive
- $\chi_{\text{H}} < \chi_{\text{O}}$ ↑ polar O-H bond → weak acid character
 - ✓ Electrophilic character
- Inter and intramolecular hydrogen bonding



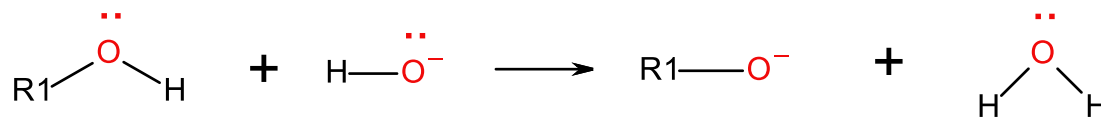
- ✓ Higher boiling and melting points than homologous alkanes
- ✓ Soluble in polar solvents
- ✓ Polar character ↓ with molecular mass
- ✓ High molar mass alcohols: amphiphiles



➤ As weak bases, protonate with strong acids



➤ As weak acids, transfer a proton to strong bases



Alcohol	Name	pK _a
	<i>tert</i> -butanol	18.0
CH ₃ -CH ₂ -OH	Ethanol	16.0
	Water	15.74
CH ₃ -OH	Methanol	15.54
	1,1,1-trifluoroethanol	12.43

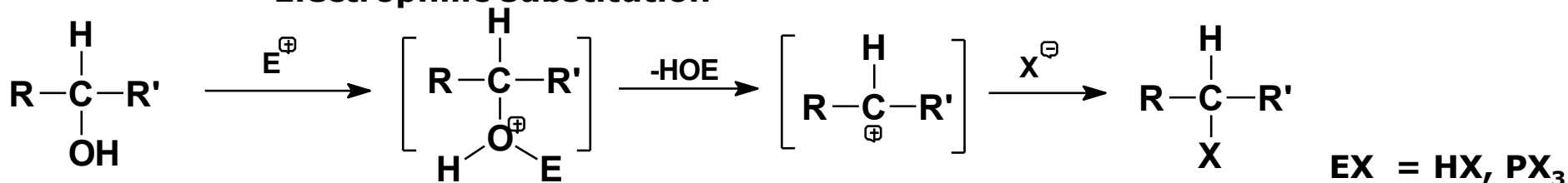
Alcohol	Name	pK _a
	<i>p</i> -aminophenol	10.46
	Phenol	9.89
	<i>p</i> -nitrophenol	7.15
	2,4,6-trinitrophenol	0.60

Where does this value come from?

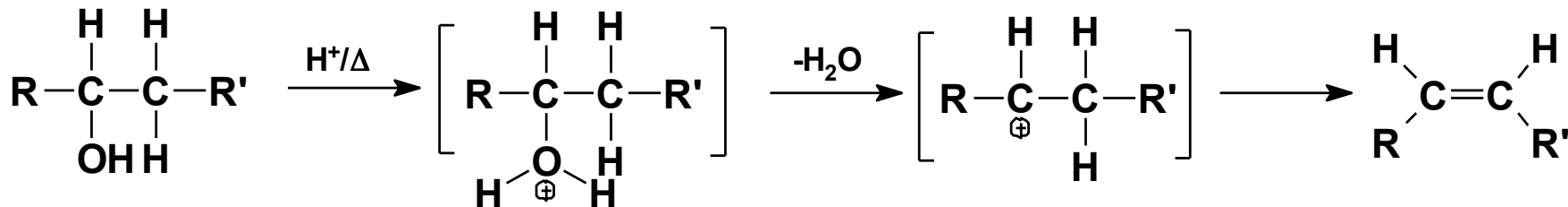
Reactivity

■ Breakdown of C-OH bond

▶ Electrophilic substitution

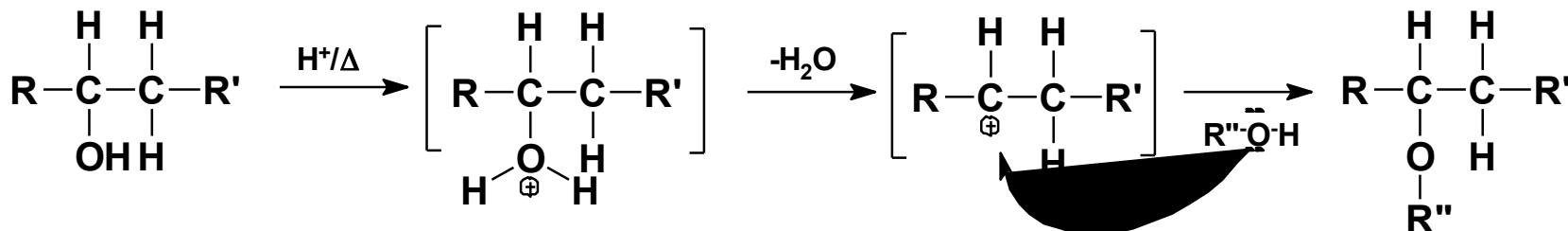


▶ Elimination: alkene formation (dehydration)



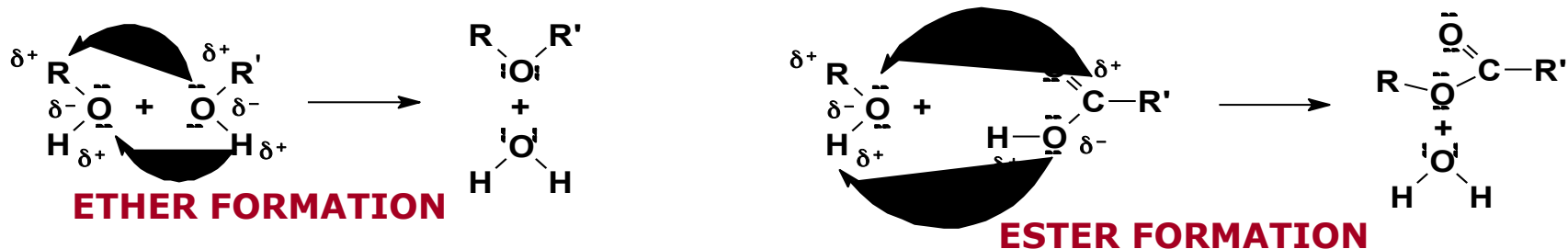
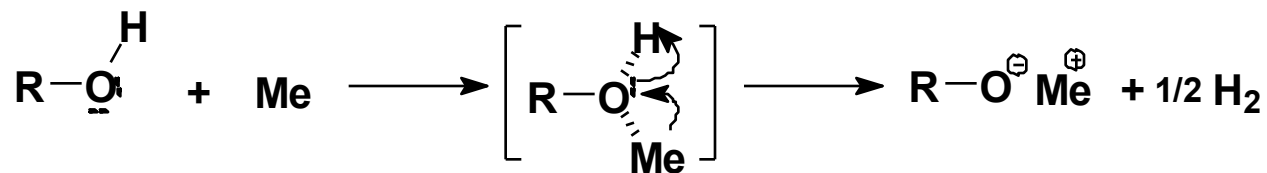
Possible transpositions. **Zaitsev rule**: the more substituted alkene is preferentially formed (the more stable)

▶ Condensation: ether formation

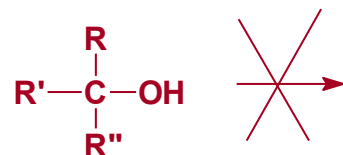
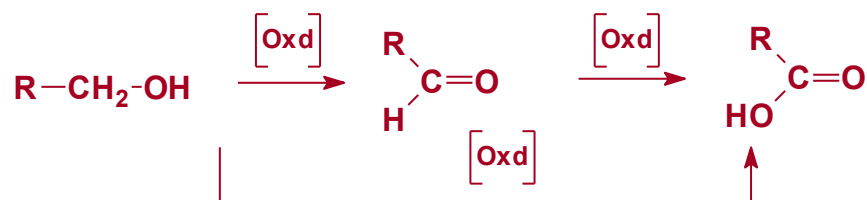


■ Breakdown of CO-H bond

▶ Electrophilic substitution (alcooxide formation)



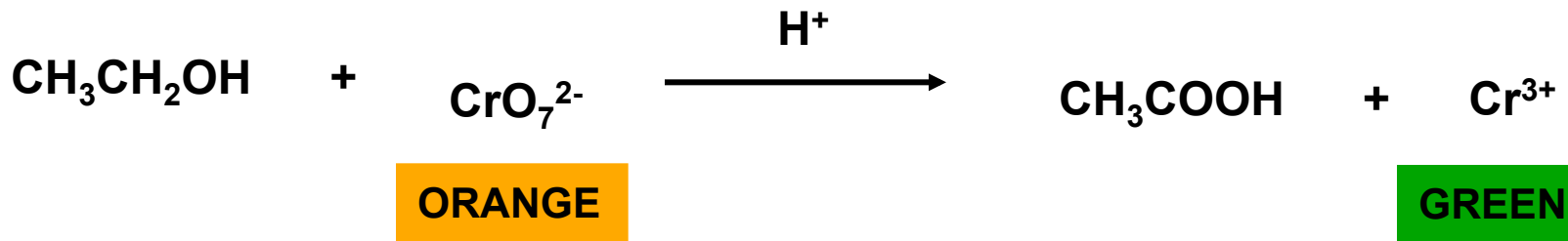
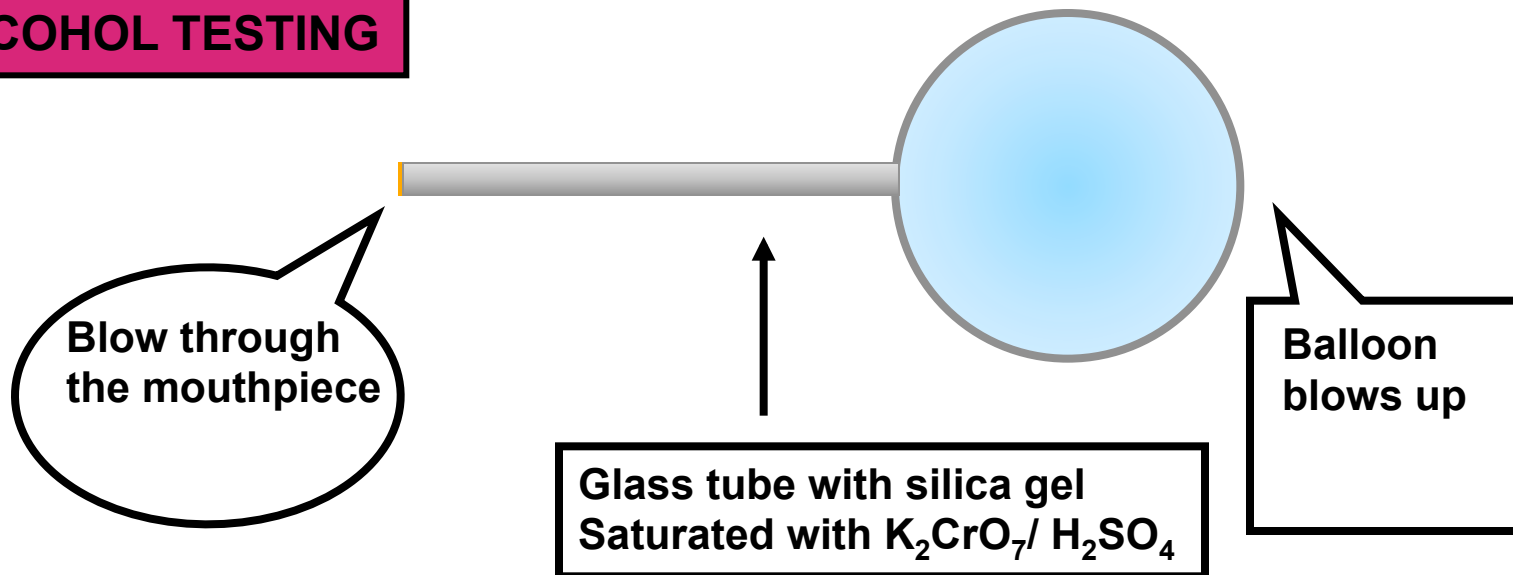
▶ Oxidation



$\text{K}_2\text{Cr}_2\text{O}_7 < \text{MnO}_4\text{K (dil)} < \text{MnO}_4\text{K}/\text{H}^+ < \text{MnO}_4\text{K}/\text{H}^+/\Delta$

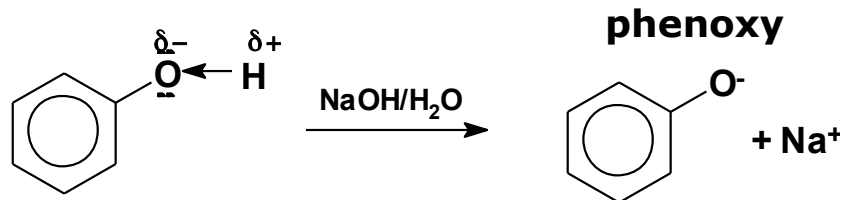
→
Oxidizing power

ALCOHOL TESTING

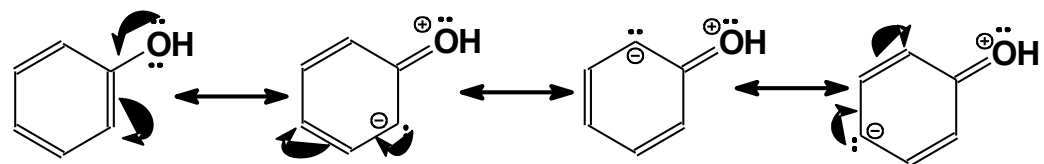


Properties

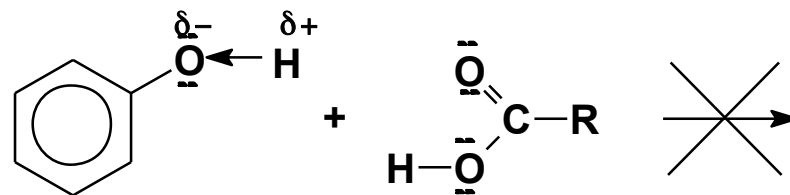
Acids



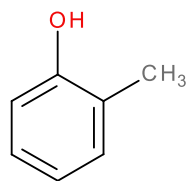
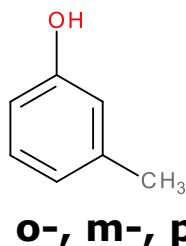
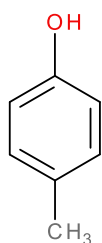
Activating agent (ortho and para)



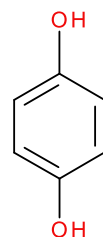
Esteric effects. Voluminous group



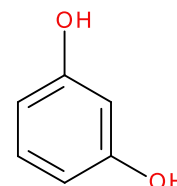
Hydrogen bonding: high boiling /melting points



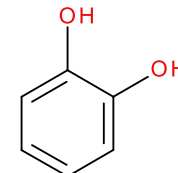
o-, m-, p-cresols



Hydroquinone

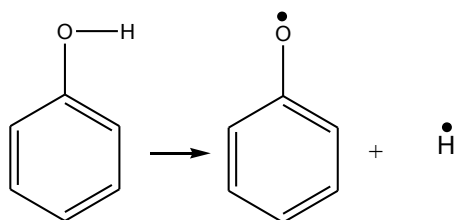


**Resorcinol,
resorcin**



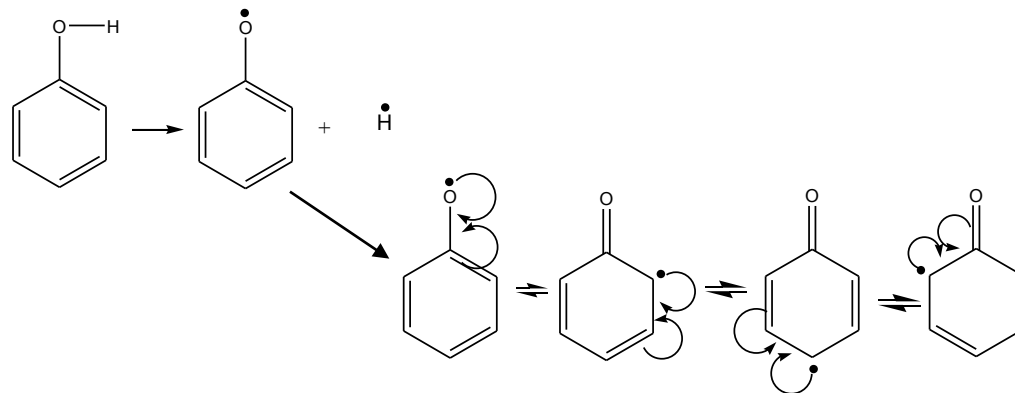
**Catechol,
pyrocatechol**

Radical scavengers

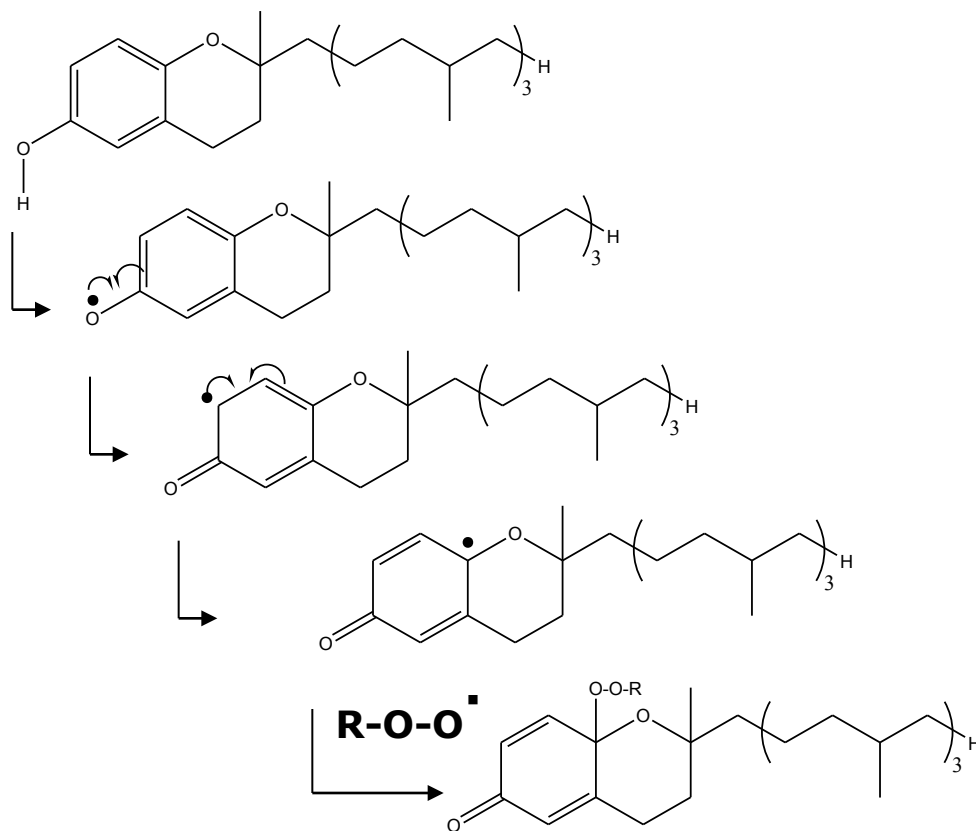


▶ Radical scavengers

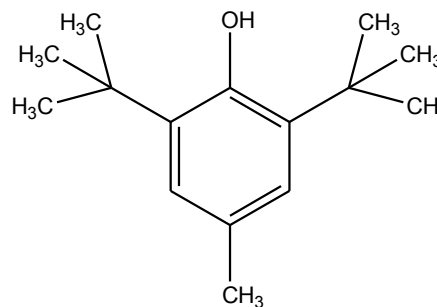
Phenoxy radical stabilizes by resonance



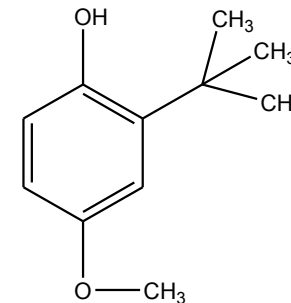
Vitamin E: antioxidant



Industrial antioxidants BHT, BHA



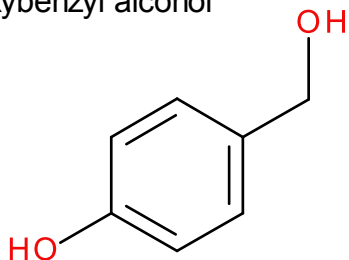
**Butylated
hydroxytoluene**



Butylated hydroxyanisole

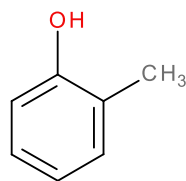
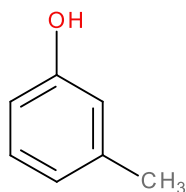
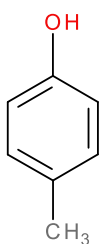
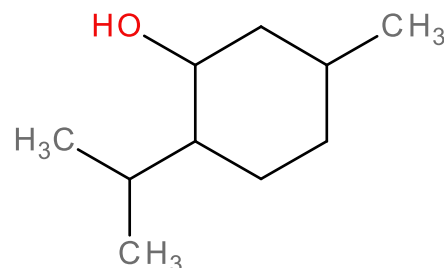
Some natural alcohols and phenols

4-hydroxybenzyl alcohol



Cofactor of indoleacetic acid oxidase

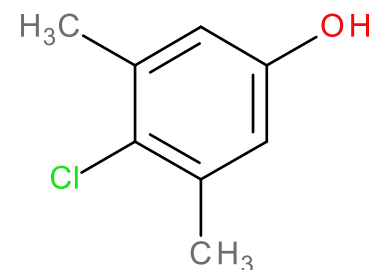
2-isopropyl-5-methyl-cyclohexanol
Menthol



o-, m-, p-cresols

Mixtures of cresols: deodorizer,
household cleaners and disinfectants
(Lysol)

4-chloro-3,5-dimethyl-phenol
Chloroxylenol (Dettol)

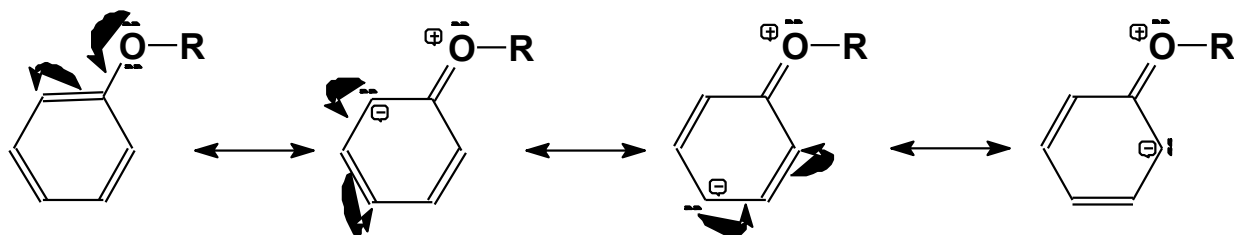


Antiseptic

Ethers(-O-)

Properties

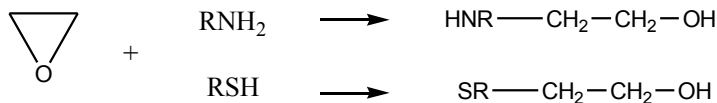
- ▶ Stable and low reactivity
- ▶ Activating agent (o- and p-)



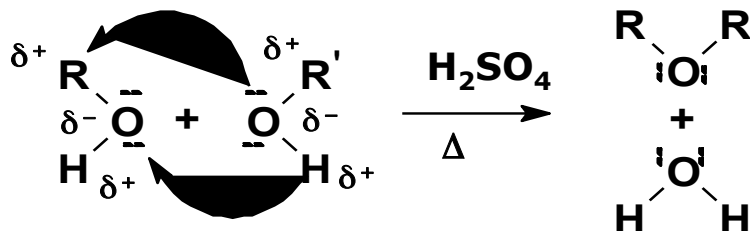
- ▶ Ethylene oxide: sterilizing agent

Reactivity

- ▶ Can form dangerous peroxides

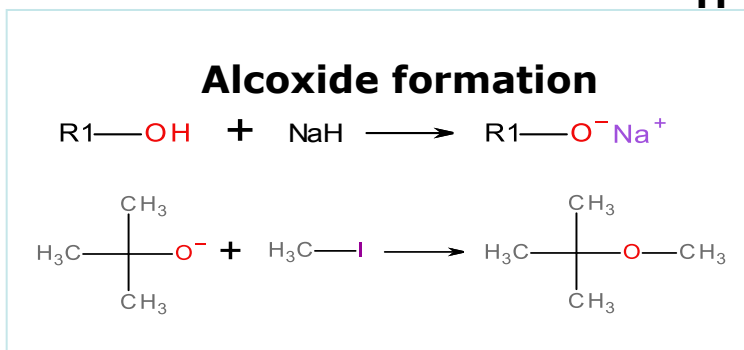


- Alcohol dehydration



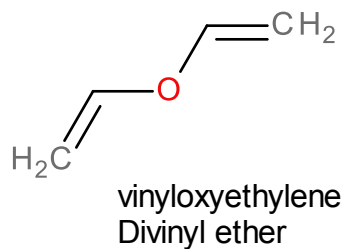
H_2SO_4 is strong
dehydrating
agent

- Williamson synthesis

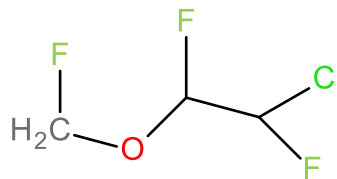


Some biologically relevant ethers

Anesthetics

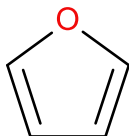


1-chloro-1,2-difluoro-2-(fluoromethoxy)ethane
Enflurane

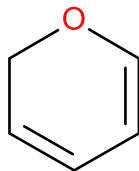


Basis for many carbohydrates and nucleic acids

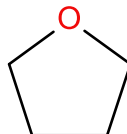
furan



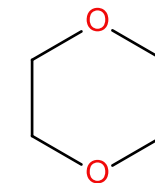
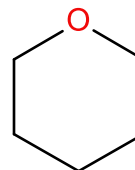
2H-pyran



tetrahydrofuran



tetrahydropyran



1,4-dioxane



Thiols(-SH)

Properties

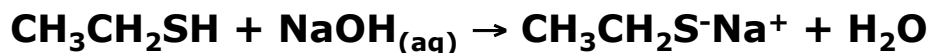
▶ **-SH sulfhydryl group bonded to a C atom**

▶ **Old literature:** mercaptan (mercury capturing); give sulfide salts in aqueous Hg^{2+} solutions

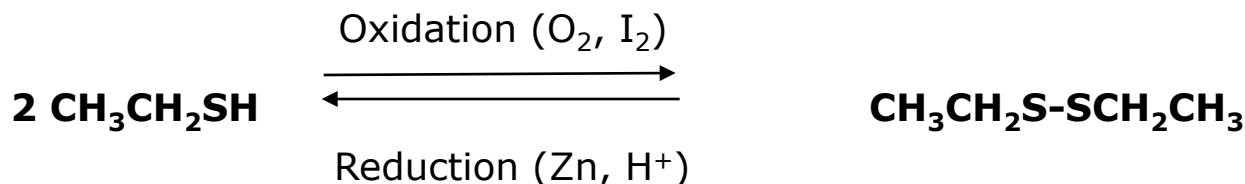
▶ $\chi_{\text{S}} = 2.5$; $\chi_{\text{H}} = 2.1$; $\chi_{\text{S}} - \chi_{\text{H}} = 0.4 \rightarrow$ **low polarity: no hydrogen bonding (boiling points of $\text{CH}_3\text{CH}_2\text{SH}$ and CH_3SCH_3 are 35 and 37°C); lower boiling points than alcohols**

Reactivity

■ **Weak acids ($\text{pK}_a \approx 10$)**

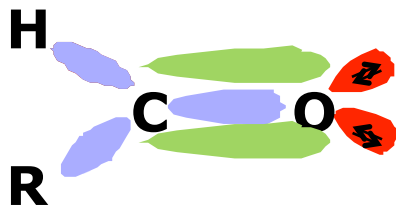


■ **Disulfide formation (R-S-S-R)**

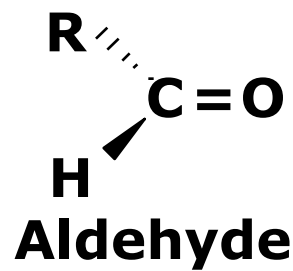
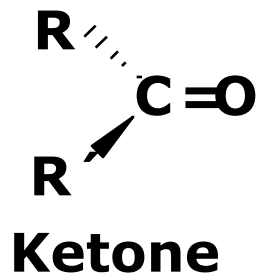


Important role in proteins

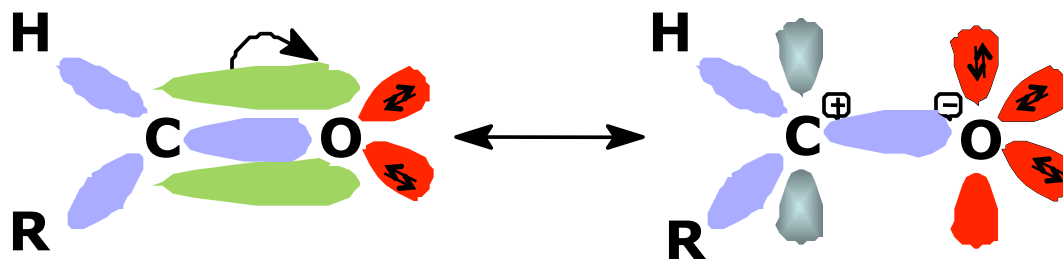
Carbonyl compounds (C=O)



Bond	C-O	C=C	C=O
E_{bond} (kcal mol ⁻¹)	84	146	176



Why are carbonyl compounds so reactive?



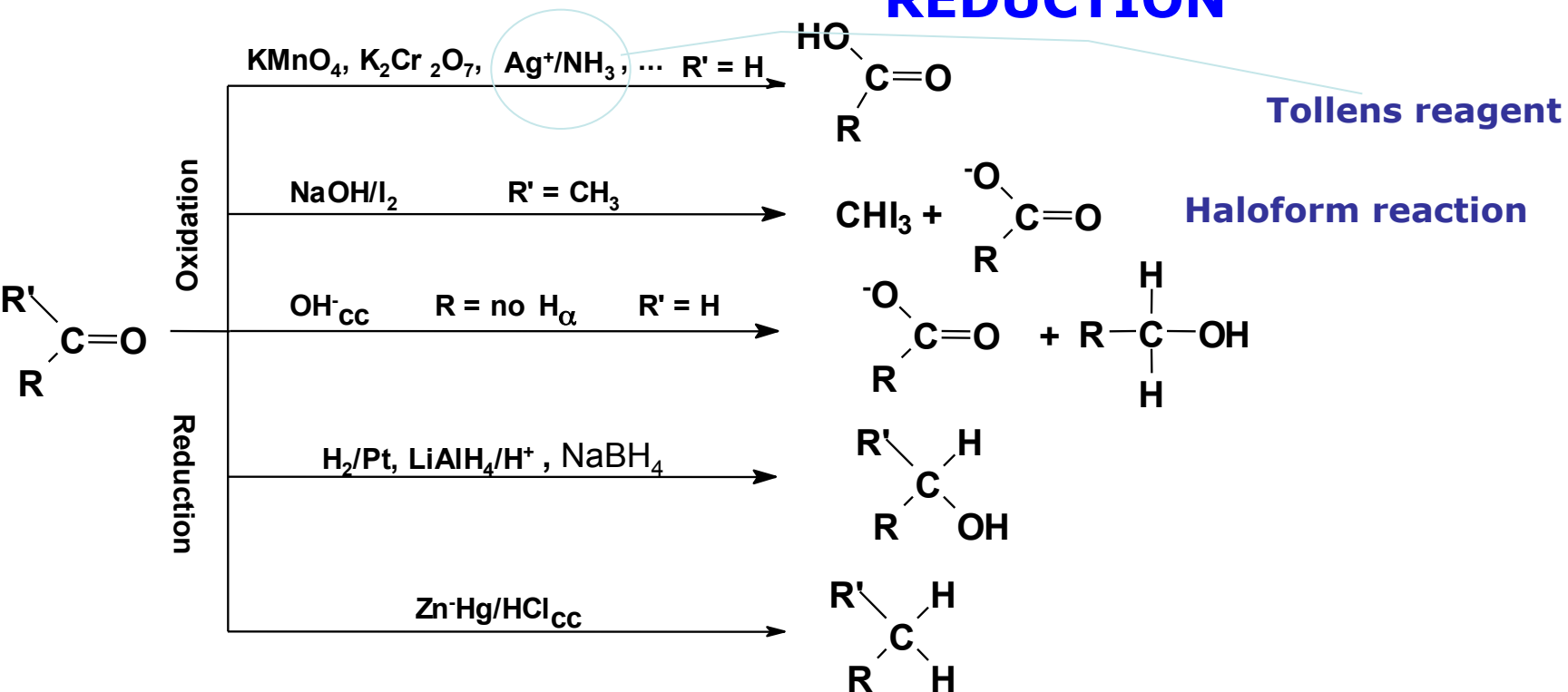
Reactivity

Oxidation-reduction

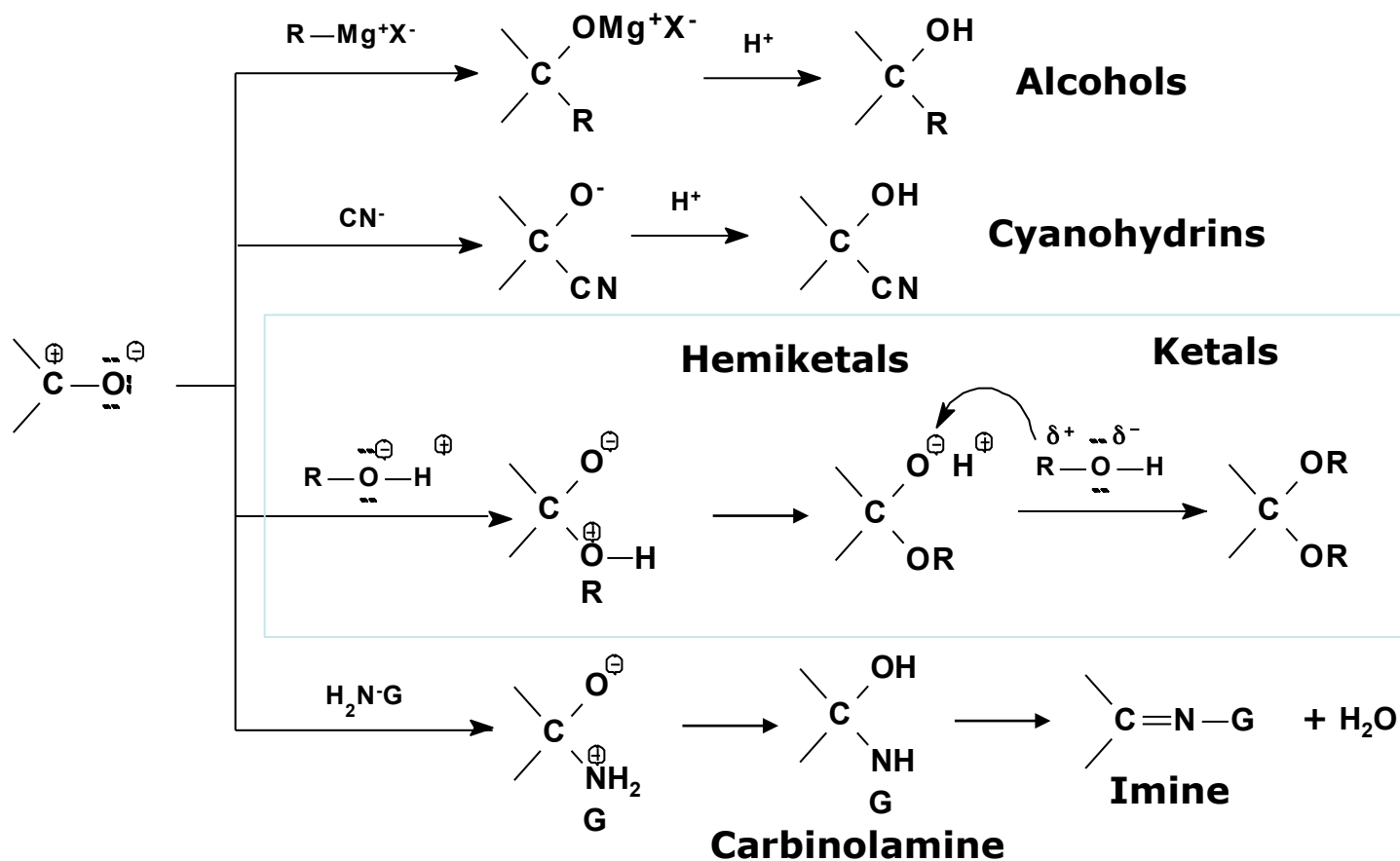
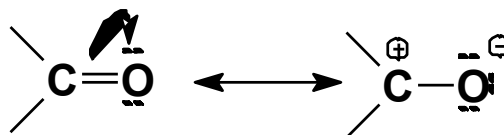
Hydrocarbons	$\text{CH}_3\text{-CH}_3$	$\text{H}_2\text{C=CH}_2$	$\text{HC}\equiv\text{CH}$	—	—
Alkyl halogenides	—	$\text{CH}_3\text{-CH}_2\text{Cl}$	$\text{CH}_3\text{-CHCl}_2$	$\text{CH}_3\text{-CCl}_3$	CCl_4
Oxygenated compounds	—	$\text{CH}_3\text{-CH}_2\text{OH}$	$\text{CH}_3\text{-CH=O}$	$\text{CH}_3\text{-COOH}$	CO_2
Nitrogenated compounds	—	$\text{CH}_3\text{-CH}_2\text{NH}_2$	$\text{CH}_3\text{-CH=NH}$	$\text{CH}_3\text{-C}\equiv\text{N}$	-

OXIDATION

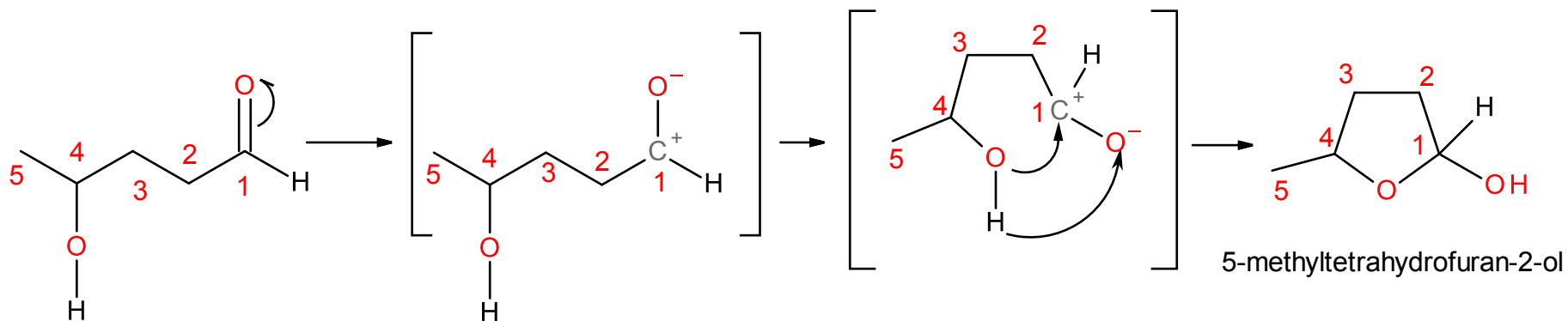
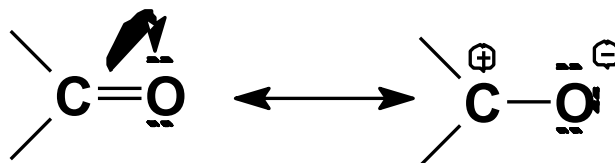
REDUCTION



► **Nucleophilic addition**

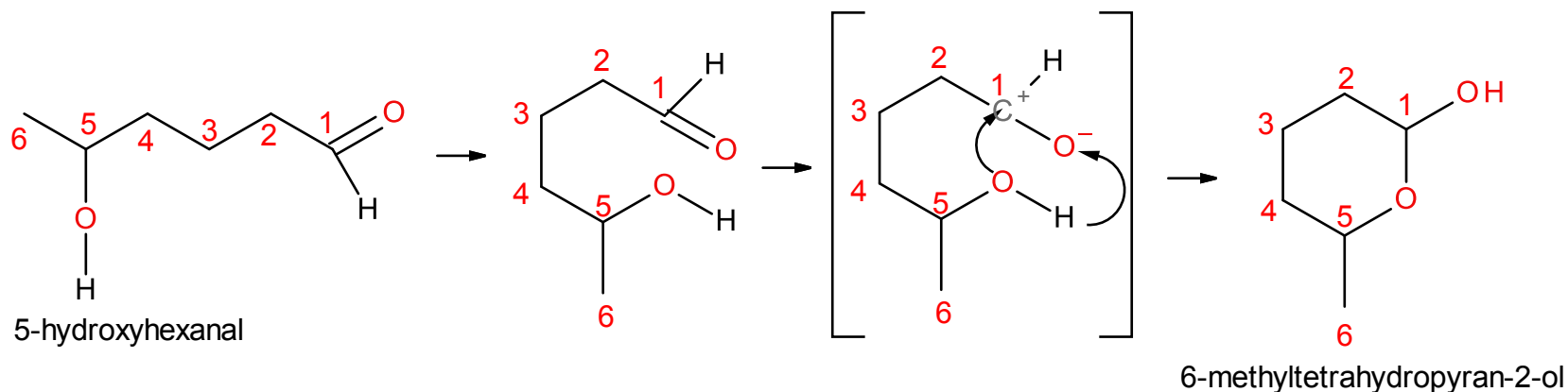


Nucleophilic self-addition



3-hydroxybutanal

Cyclic hemiacetal. Five membered: furan-



5-hydroxyhexanal

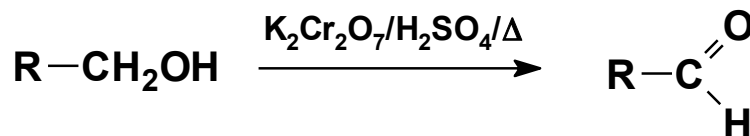
6-methyltetrahydropyran-2-ol

Cyclic hemiacetal. Six membered: pyran-

Synthesis

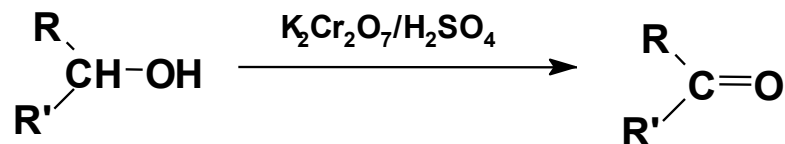
Aldehydes

- Oxidation of primary alcohols

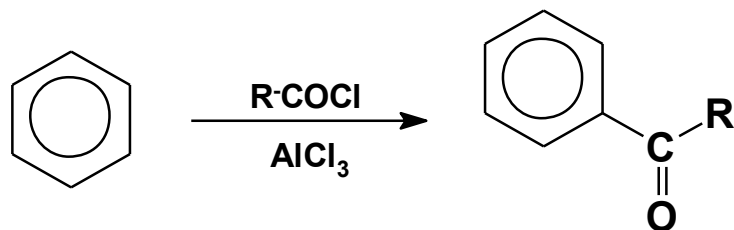


Ketones

- Oxidation of secondary alcohols

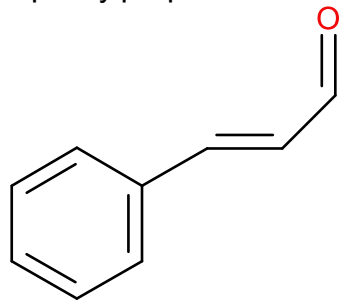


- Friedel-Crafts acylation



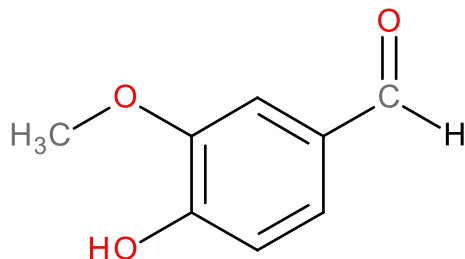
Natural aldehydes and ketones

(E)-3-phenylprop-2-enal



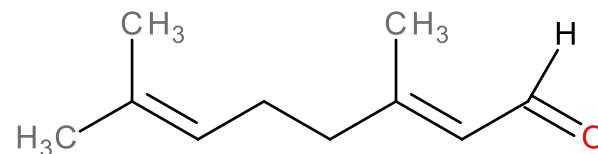
Cinnamaldehyde
Cinnamon oil

4-hydroxy-3-methoxy-benzaldehyde



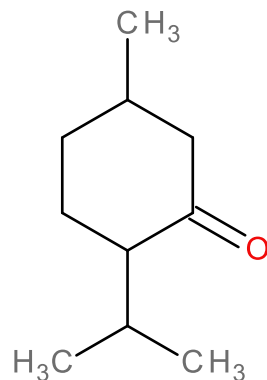
Vanilla

(2E)-3,7-dimethylocta-2,6-dienal



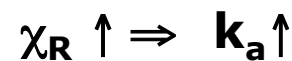
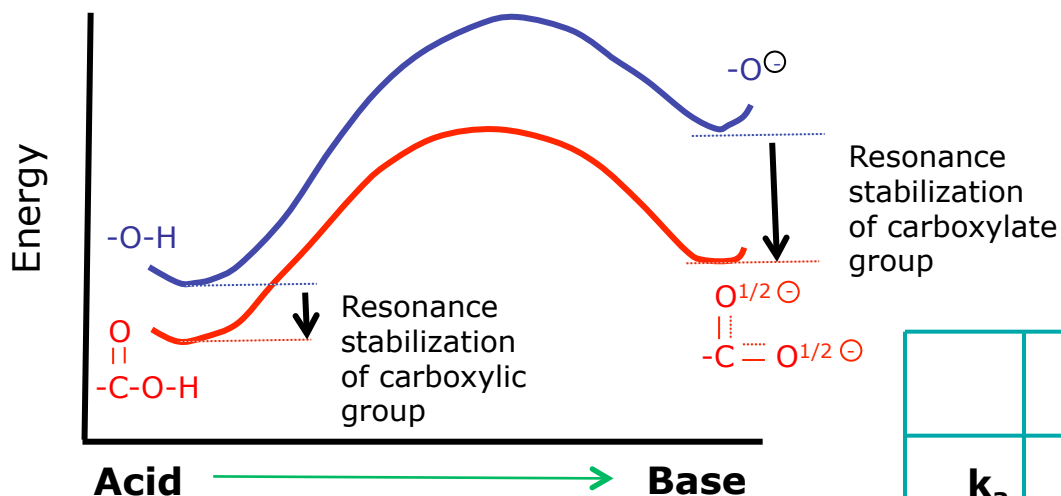
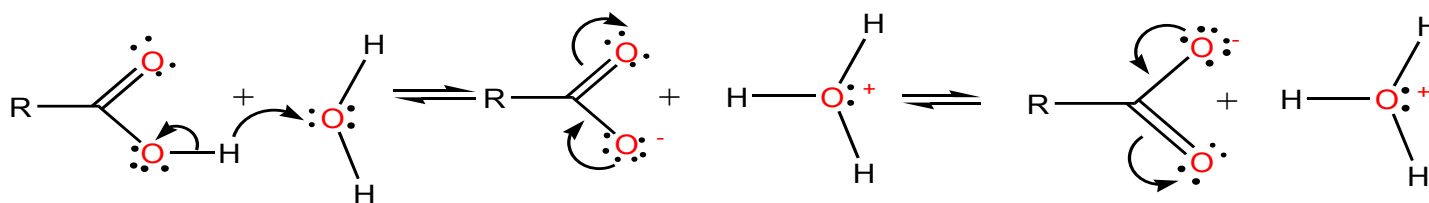
Rinds of citrus fruit

2-isopropyl-5-methyl-cyclohexanone

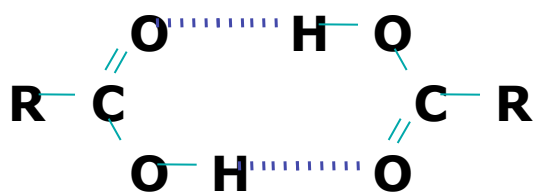


Mint plants

Carboxylic compounds (-COOH)



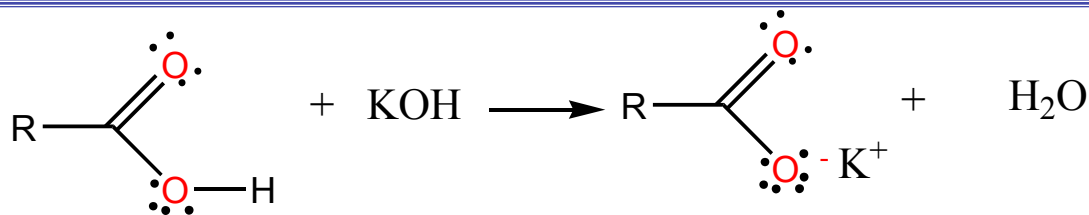
	<chem>CICH2COOH</chem>	<chem>Cl2CHCOOH</chem>	<chem>Cl3CCOOH</chem>
k_a	10^{-3}	10^{-2}	10^{-1}



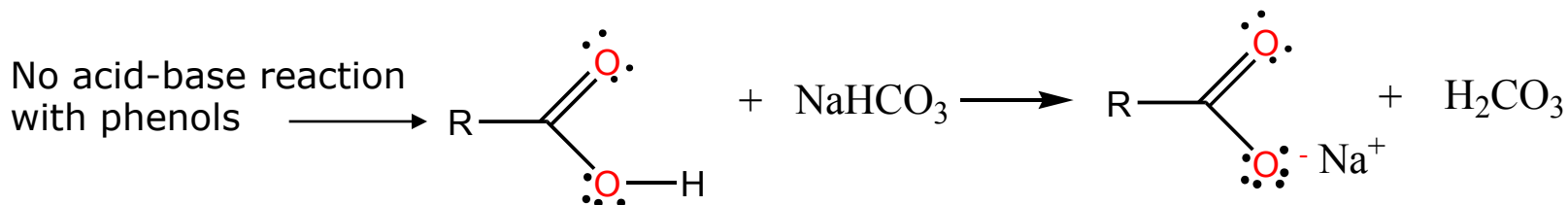
- Higher T_m and T_b than alcohols
- Soluble in water up to C_5

Reactivity

Acid base reactions:



No acid-base reaction
with phenols

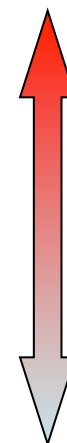


Acid

pK_a

F ₃ C-COOH	0.23
FCH ₂ -COOH	2.59
ClCH ₂ -COOH	2.85
BrCH ₂ -COOH	2.68
ICH ₂ -COOH	3.12
H-COOH	3.75
HOCH ₂ -COOH	3.83
C ₆ H ₅ -COOH	4.19
CH ₃ -COOH	4.75
CH ₃ CH ₂ -COOH	4.87

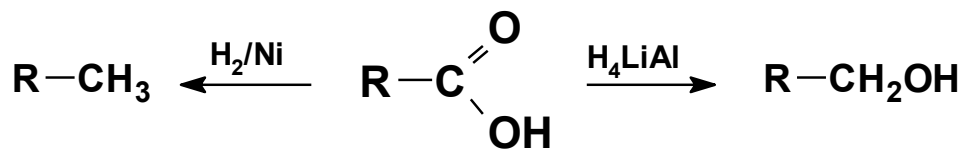
Strong acid



Weak acid

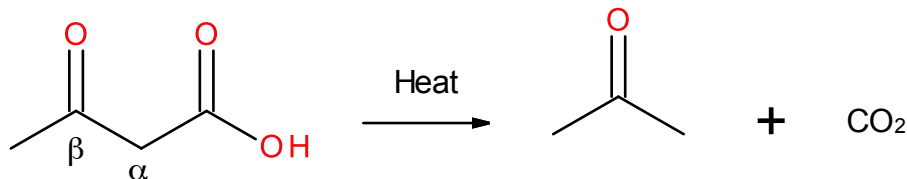
Comparing the three pointed acids study the electron withdrawing or releasing effect of -CH₃, -C₆H₅

Reduction reactions

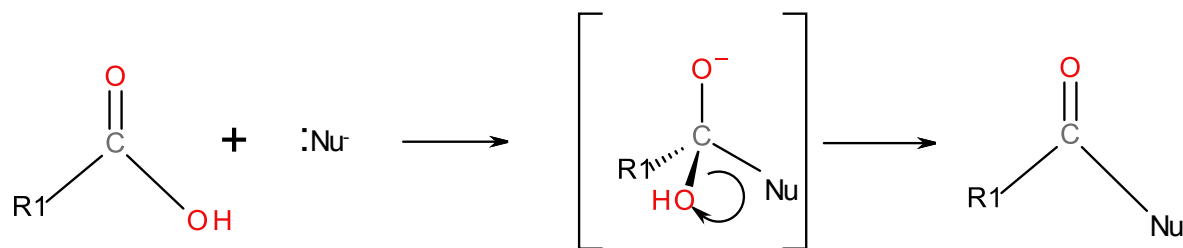


▶ Decarboxylation

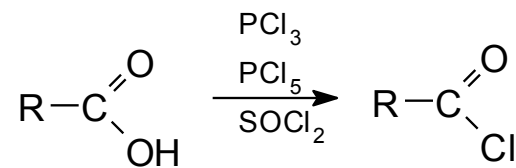
Common carboxylic acids are thermally resistant. Exceptions are β -ketocarboxylic acids



▶ Nucleophilic substitution

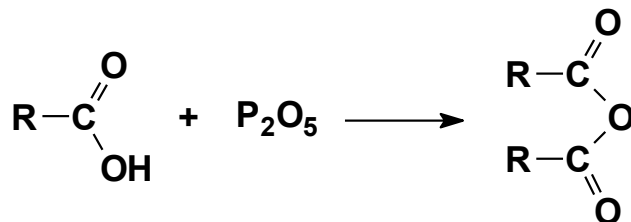


▶ Formation of acid (acyl) halogenides

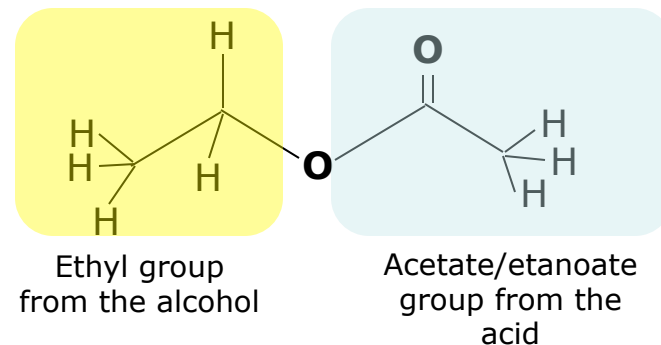
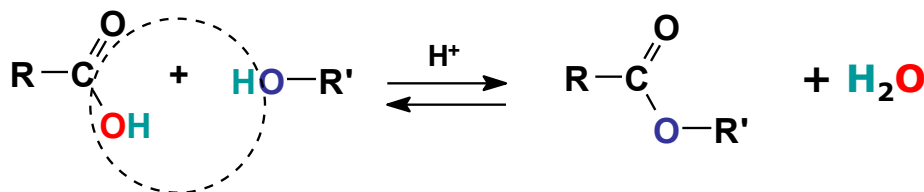


► Nucleophilic substitution

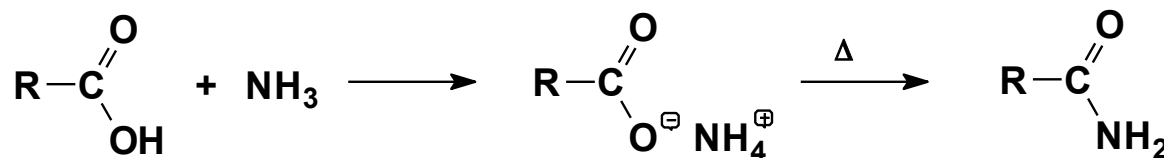
► Anhydrides



► Esterification

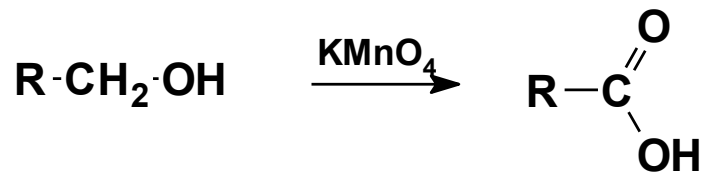


► Formation of amides

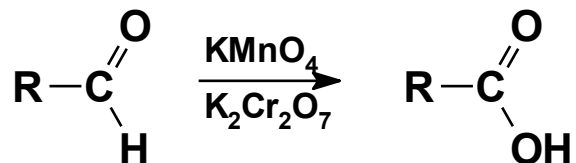


Synthesis

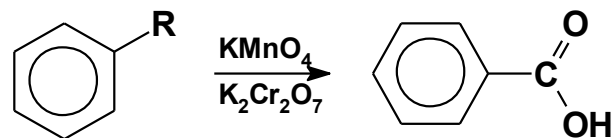
- Primary alcohol oxidation



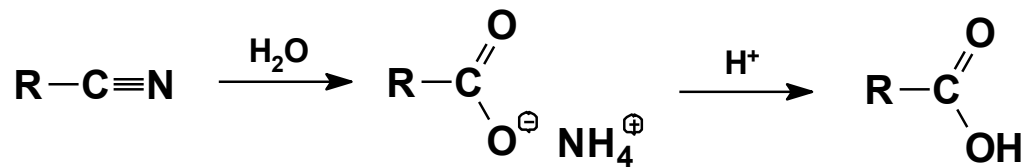
- Aldehyde oxidation



- Alkyl benzene oxidation



- Nitrile hydrolysis





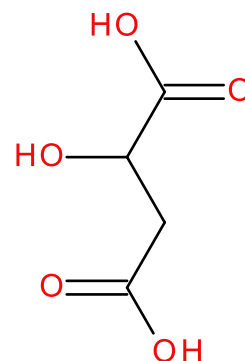
Natural carboxylic acids

Formula	Common Name	Source	IUPAC Name	Melting Point	Boiling Point
HCO ₂ H	formic acid	ants (L. formica)	methanoic acid	8.4 °C	101 °C
CH ₃ CO ₂ H	acetic acid	vinegar (L. acetum)	ethanoic acid	16.6 °C	118 °C
CH ₃ CH ₂ CO ₂ H	propionic acid	milk (Gk. protus prion)	propanoic acid	-20.8 °C	141 °C
CH ₃ (CH ₂) ₂ CO ₂ H	butyric acid	butter (L. butyrum)	butanoic acid	-5.5 °C	164 °C
CH ₃ (CH ₂) ₃ CO ₂ H	valeric acid	valerian root	pentanoic acid	-34.5 °C	186 °C
CH ₃ (CH ₂) ₄ CO ₂ H	caproic acid	goats (L. caper)	hexanoic acid	-4.0 °C	205 °C
CH ₃ (CH ₂) ₅ CO ₂ H	enanthic acid	vines (Gk. oenanthe)	heptanoic acid	-7.5 °C	223 °C
CH ₃ (CH ₂) ₆ CO ₂ H	caprylic acid	goats (L. caper)	octanoic acid	16.3 °C	239 °C
CH ₃ (CH ₂) ₇ CO ₂ H	pelargonic acid	pelargonium (an herb)	nonanoic acid	12.0 °C	253 °C
CH ₃ (CH ₂) ₈ CO ₂ H	capric acid	goats (L. caper)	decanoic acid	31.0 °C	219 °C

Natural carboxylic acids

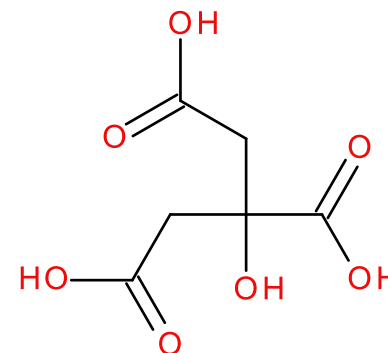
Saturated fatty acids

Formula	Common Name	Melting Point
$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$	lauric acid	45 °C
$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$	myristic acid	55 °C
$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$	palmitic acid	63 °C
$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$	stearic acid	69 °C
$\text{CH}_3(\text{CH}_2)_{18}\text{CO}_2\text{H}$	arachidic acid	76 °C

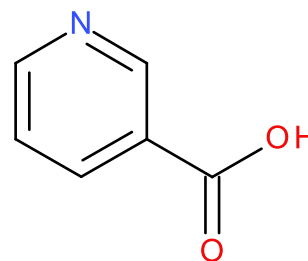


2-hydroxybutanedioic acid
Malic acid

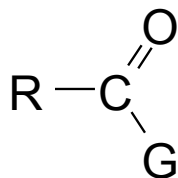
citric acid



nicotinic acid

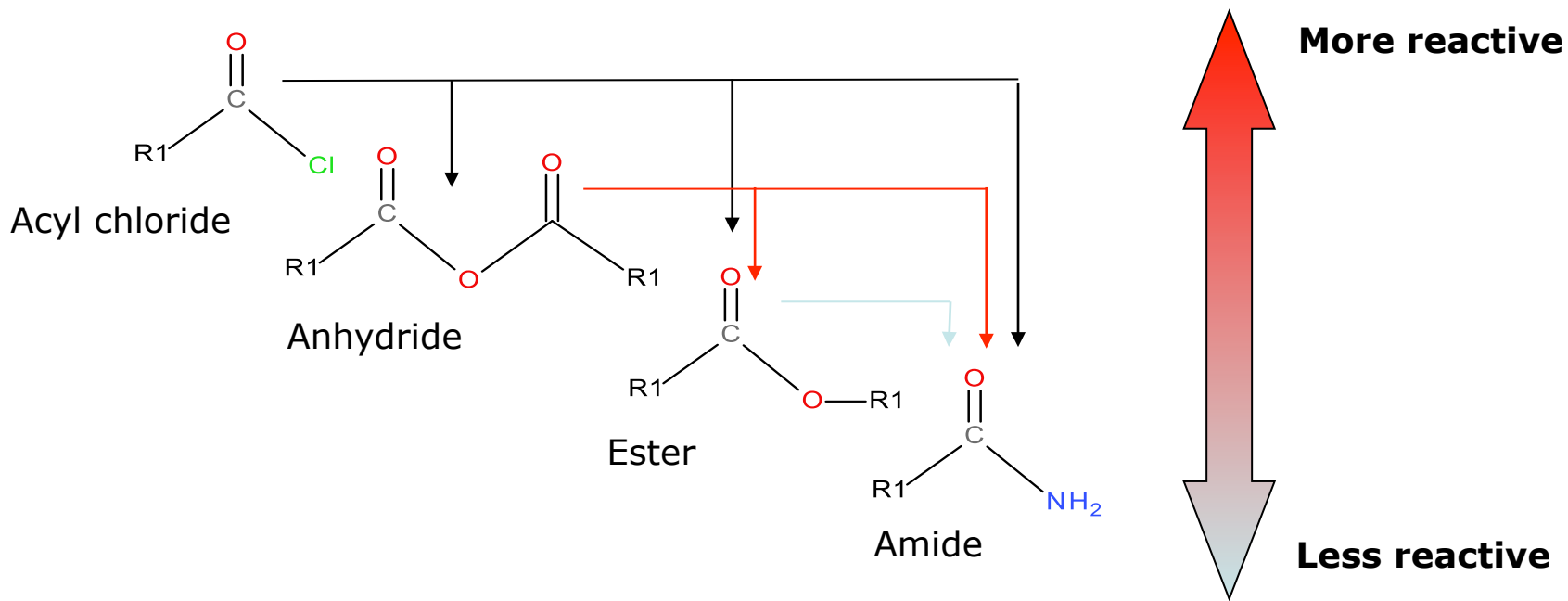


Derivatives of carboxylic acids (-COOH)



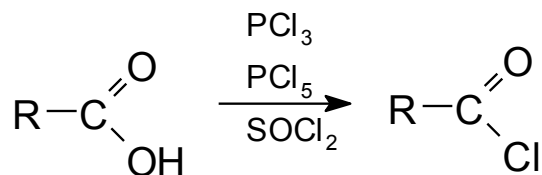
Inter-conversion between carboxylic derivatives

The higher the electronegativity of substituent, the less stable de derivative

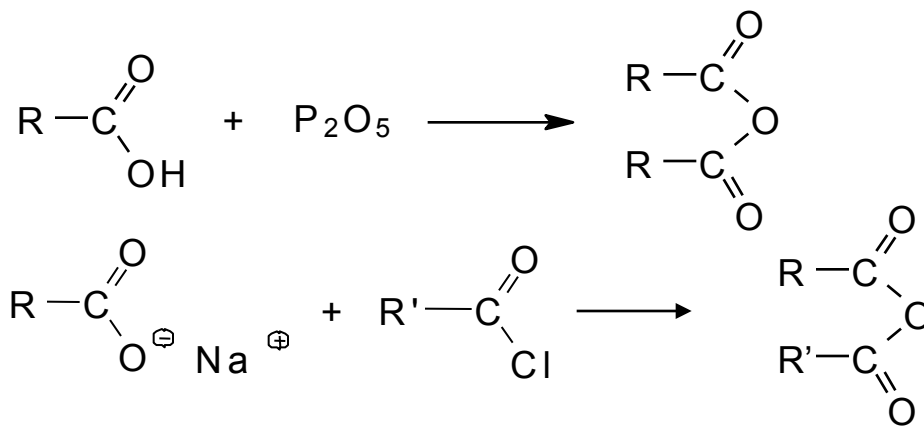


Synthesis

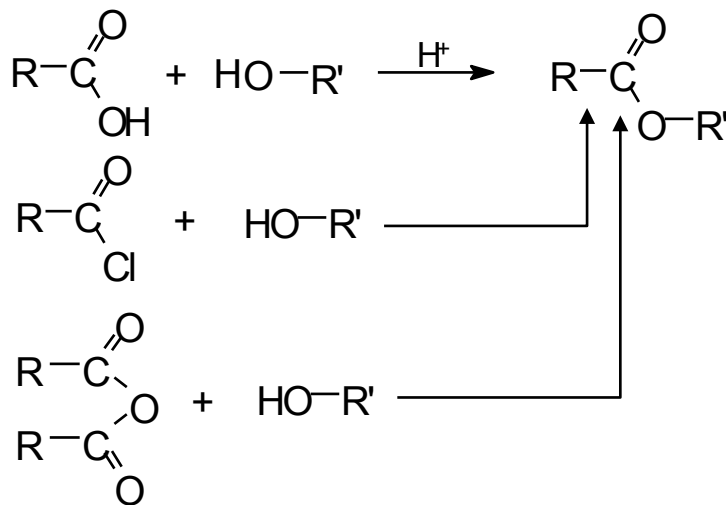
➤ Acid halogenides



➤ Anhydrides

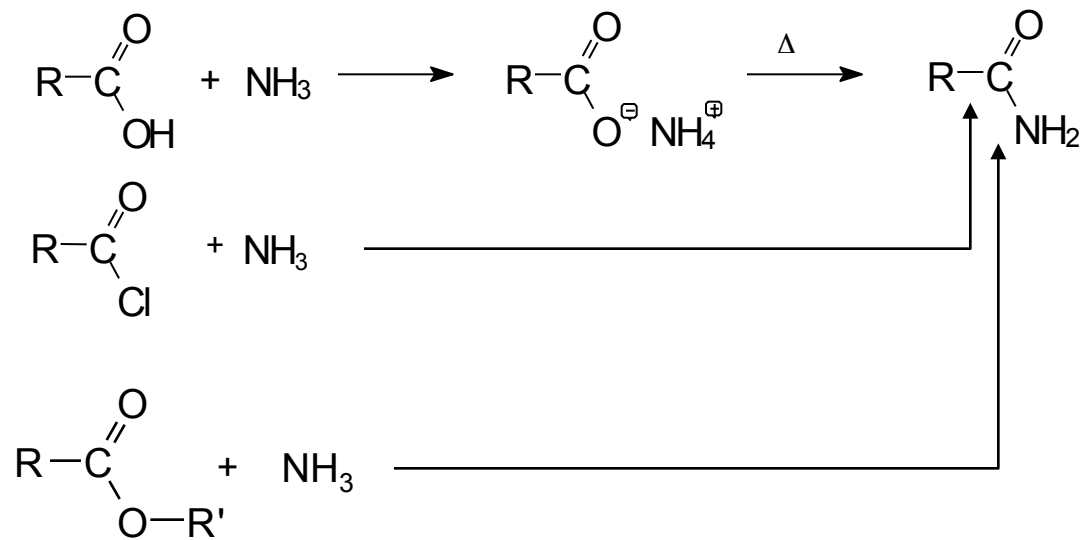


➤ Esters



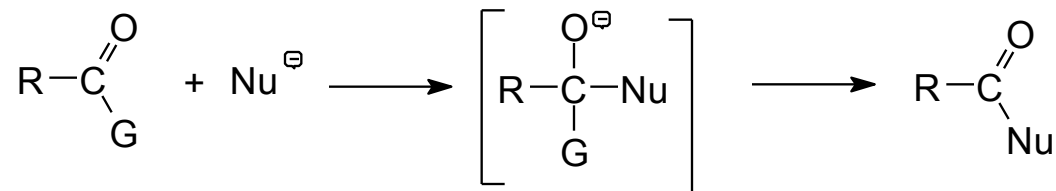


➤ Amides



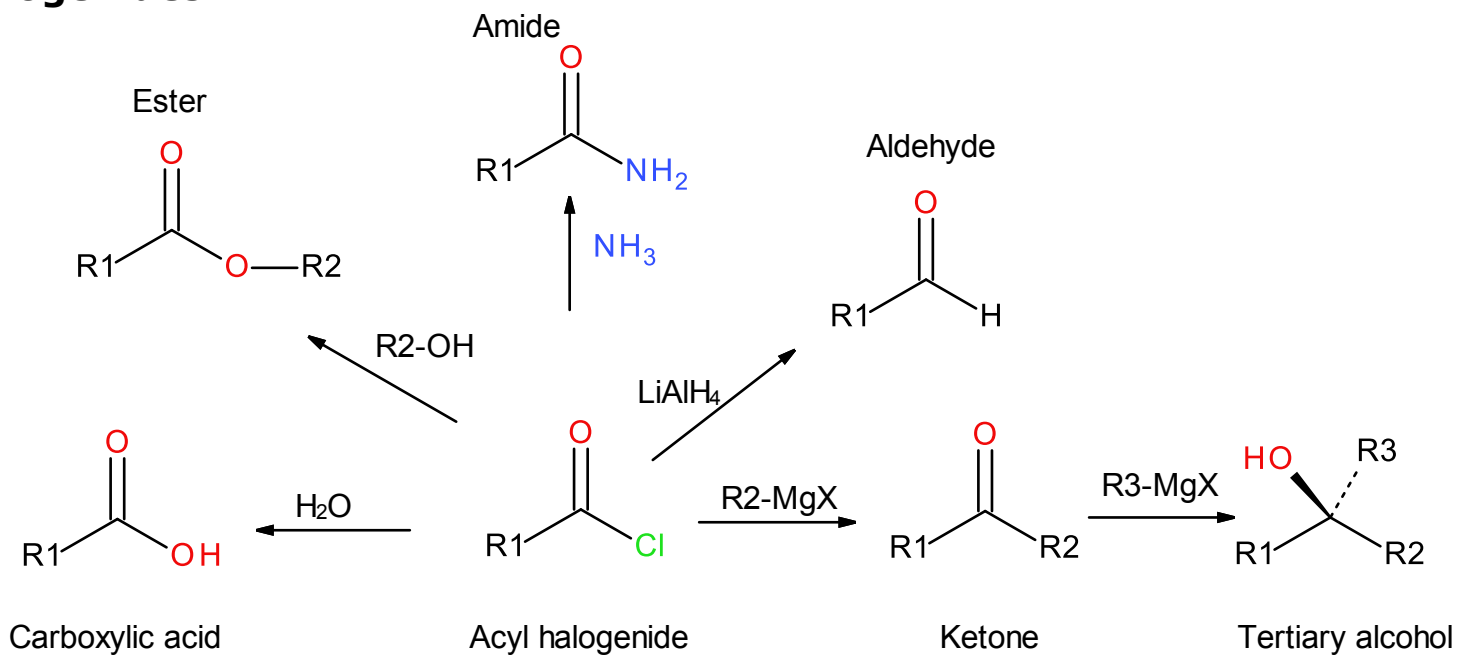
Reactivity

➤ Nucleophilic substitution



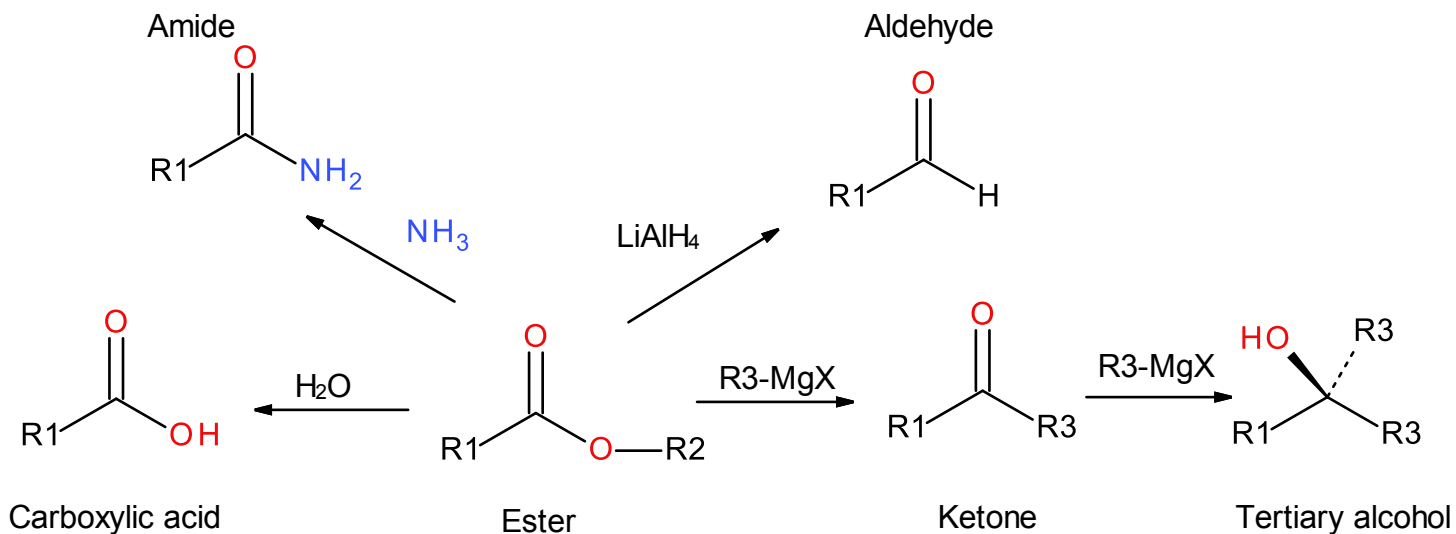
Reactivity: -Cl > R-COO- > -RO > -NH₂

○ Acid halogenides

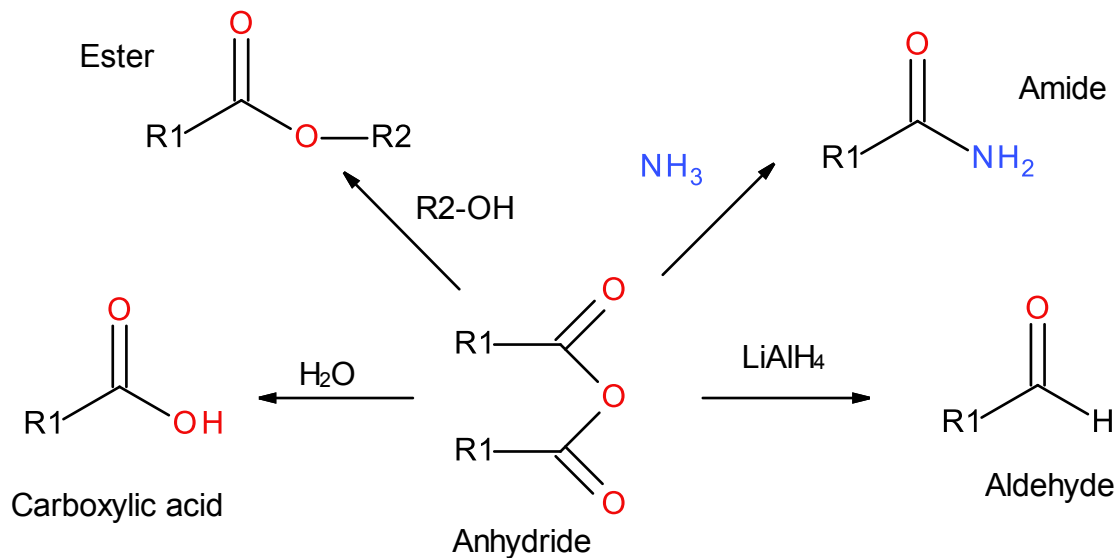




○ Esters

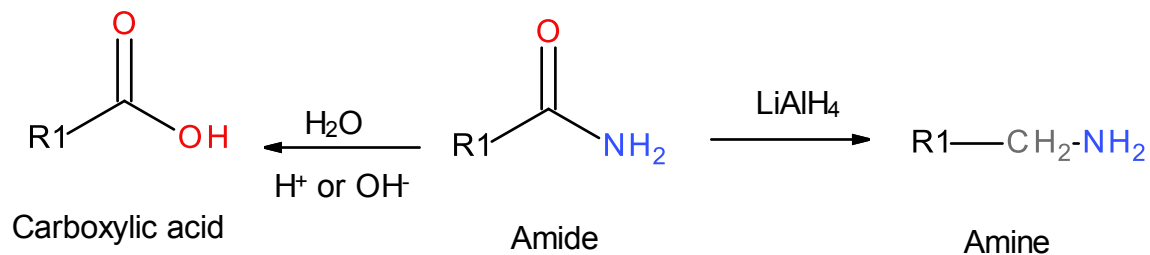


○ Anhydrides

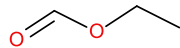
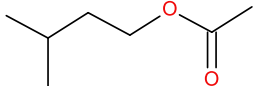
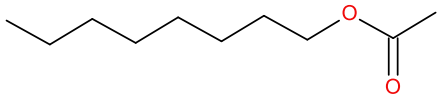
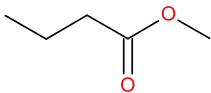
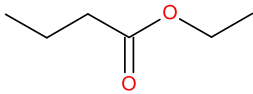
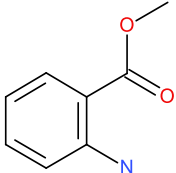




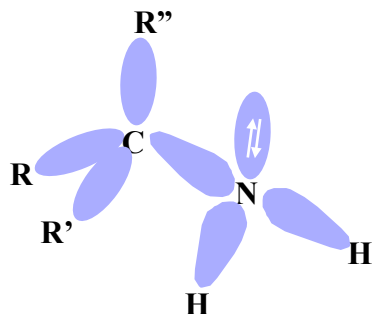
O Amides



Esters as flavoring agents

Structure	Name	Flavour
	Ethyl formate	Rum
	Isopentyl acetate	Banana
	Octyl acetate	Orange
	Methyl butanoate	Apple
	Ethyl butanoate	Pineapple
	Methyl 2-aminobenzoate	Grape

Amines (-NH₂)

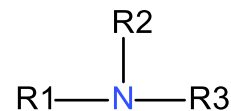
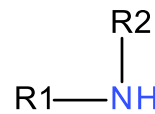
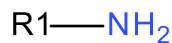


General properties

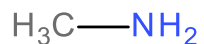
- Lone pair: basicity
- Hydrogen bonding: high boiling points
- Unpleasant odor

Classification

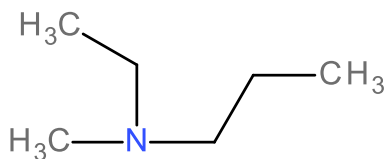
Primary, secondary, tertiary



Alkylamines, arylamines, heterocyclic amines

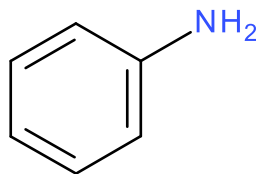


methanamine

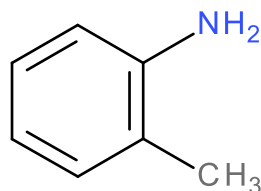


N-ethyl-N-methylpropan-1-amine

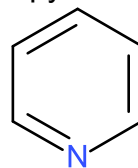
aniline



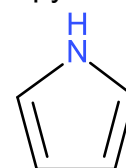
2-methylaniline



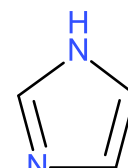
pyridine



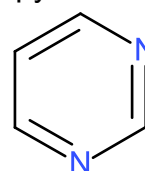
pyrrole



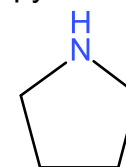
imidazole



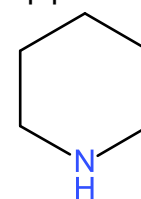
pyrimidine



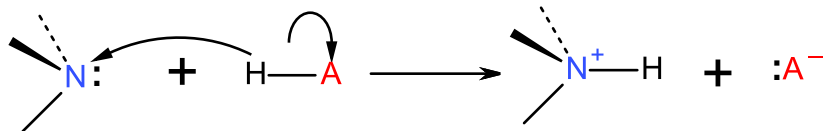
pyrrolidine



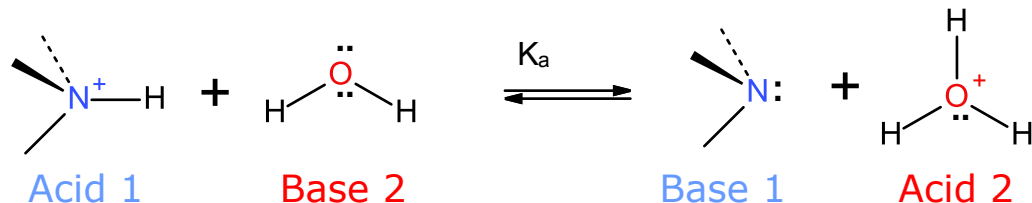
piperidine



Basicity



It is usually measured not through pK_b but through pK_a of the ammonium cation



The larger K_a (lower pK_a), ammonium cation is more acidic and less basic the conjugated amine is

		pK_a
NH_3	Ammonia	9.26
CH_3-NH_2	Methylamine	10.66
	Pyrrolidine	11.27
$(CH_3)_2-NH_2$	Dimethylamine	10.49
$(CH_3)_3-NH_2$	Trimethylamine	9.81
$(CH_3 CH_2)_3-NH_2$	Triethylamine	11.01

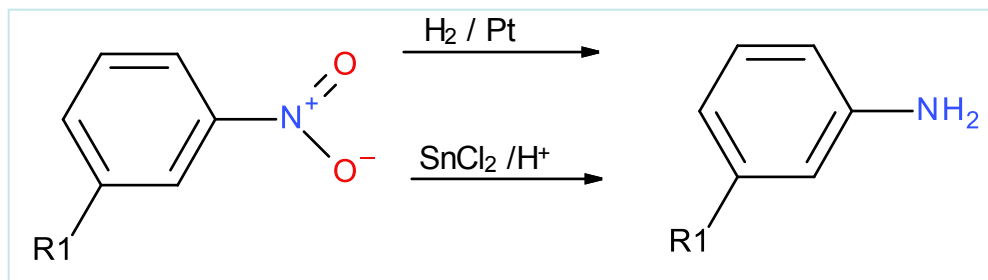
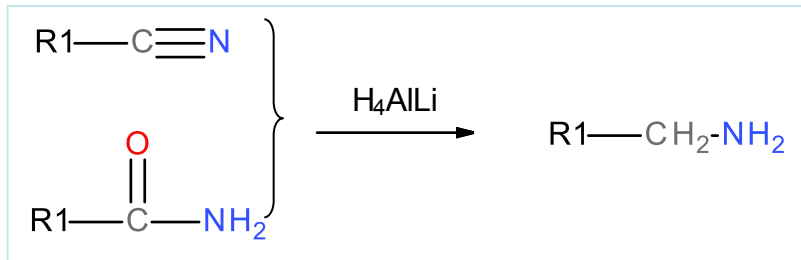
		pK_a
	Aniline	4.63
	Pyridine	5.25
	Pyrimidine	1.23
	Pyrrol	0.40

Alkyl amines are more basic than ammonia

Aromatic and heterocyclic amines very weak bases: electron pair delocalized in the aromatic ring \rightarrow less available for donation

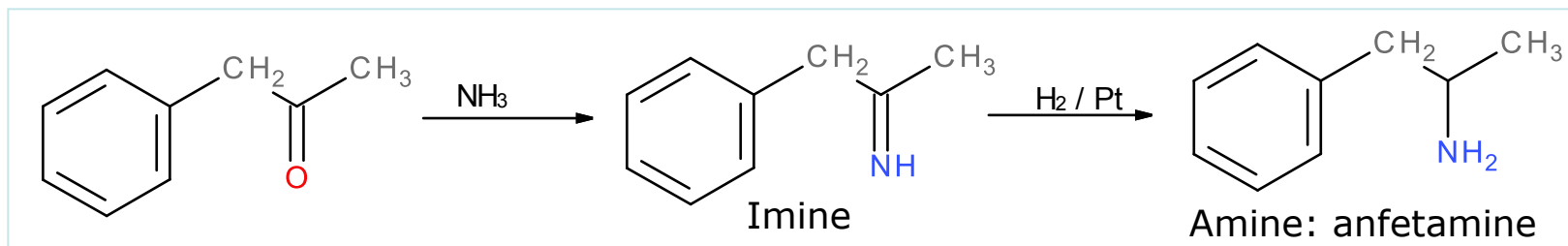
Synthesis

➤ Reduction of nitriles, amides and nitro compounds



Selection of the reducing agent depends on protection of R1

➤ Reductive amination of aldehydes and ketones



Reactivity

• Acylation

