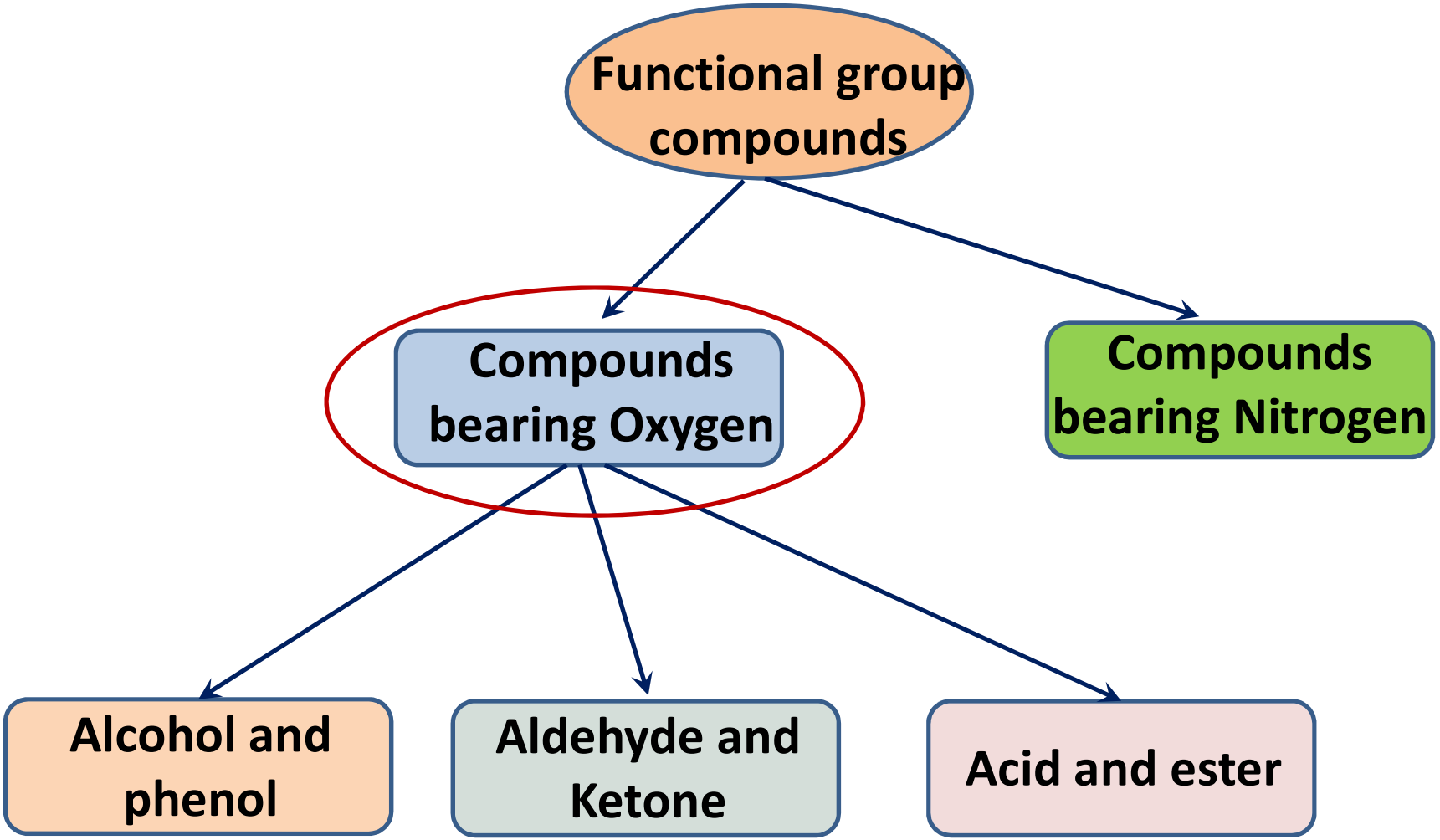
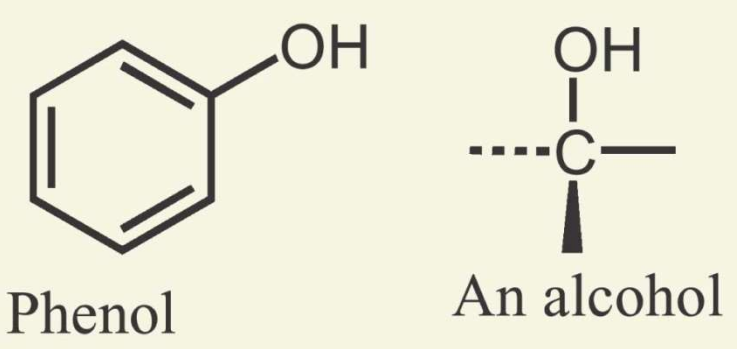
Chapter 4: Compounds bearing Oxygen



1. Alcohols and Phenols

- Alcohols contain an **OH group** connected to a **saturated C** (sp^3). General formula of aliphatic alcohol is **ROH**.

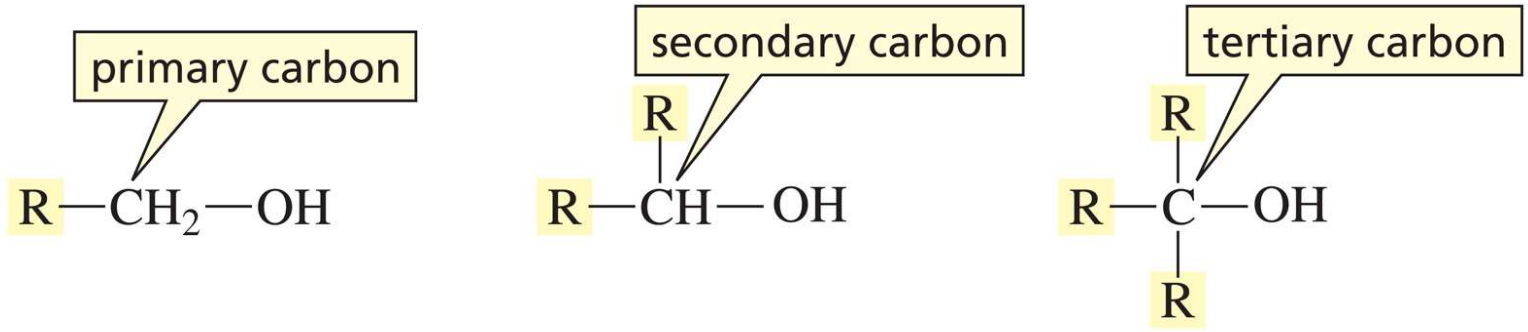
- Phenols contain an **OH group** connected to a carbon in a **benzene** ring or called Aromatic alcohols



Phenol An alcohol

Classification of Alcohols

- **Primary**: Carbon with —OH is bonded to one other carbon.
- **Secondary**: Carbon with —OH is bonded to two other carbons.
- **Tertiary**: Carbon with —OH is bonded to three other carbons.



a primary alcohol a secondary alcohol a tertiary alcohol

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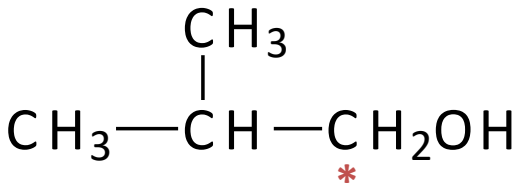
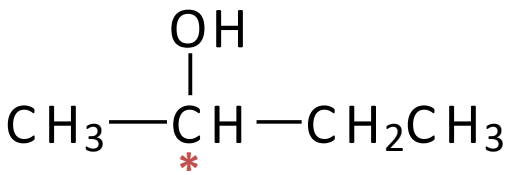
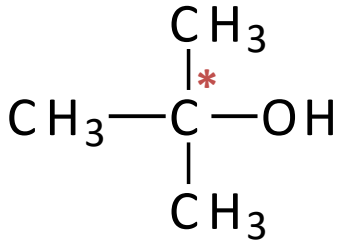


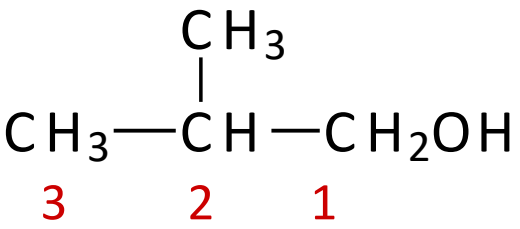




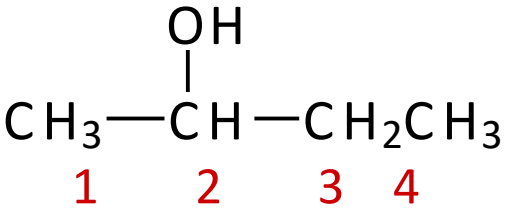
IUPAC (Systematic) Nomenclature

Method

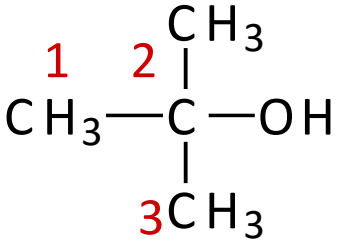
- Find the **longest** carbon chain containing the carbon with the —OH group.
- Drop the ***"–e"*** from the alkane name; add ***"–ol"***.
- Number the chain, giving the —OH group the **lowest** number possible.
- Number and name all substituents and write them in **alphabetical** order.



Old: 2-methyl-1-propanol
New: 2-methylpropan-1-ol



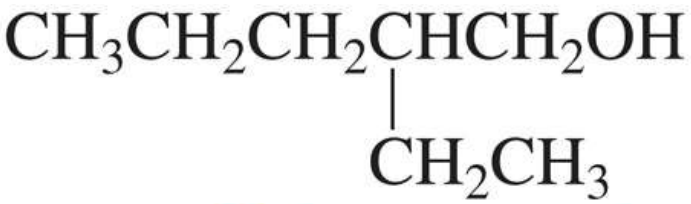
Old: 2-butanol
New: butan-2-ol



Old: 2-methyl-2-propanol
New: 2-methylpropan-2-ol

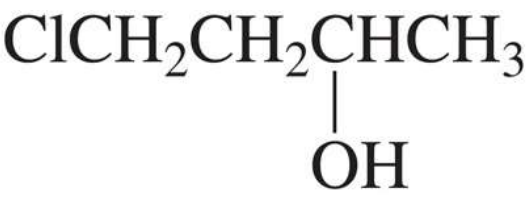
Examples

2-butanol



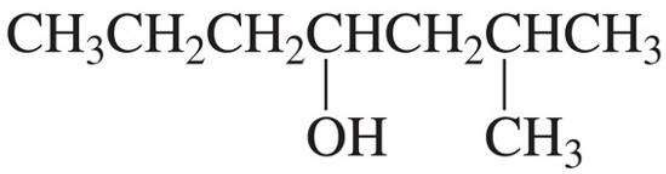
2-ethyl-1-pentanol

3-bromo-1-propanol

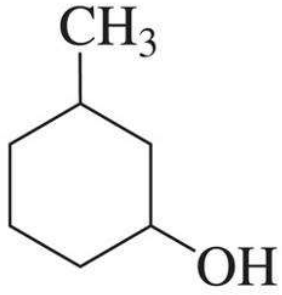


4-chloro-2-butanol

2-chloro-3-pentanol



2-methyl-4-heptanol



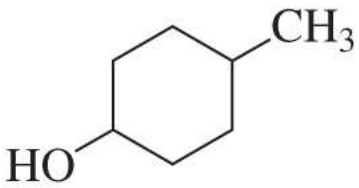
3-methylcyclohexanol

Examples

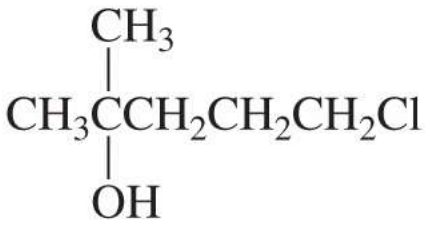
Give each of the following compounds a systematic name, and indicate whether each is a primary, secondary, or tertiary alcohol:

a. $CH_3CH_2CH_2CH_2CH_2OH$

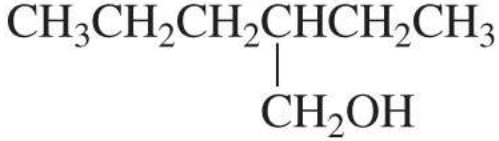
b.



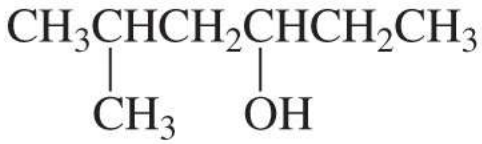
c.



d.



e.



f.

Write the structures of all the tertiary alcohols with molecular formula $C_6H_{14}O$, and give each a systematic name.

Common names of alcohol

- **Common names** are the name of alkyl group followed by the word "alcohol"
- Useful only for small alkyl groups

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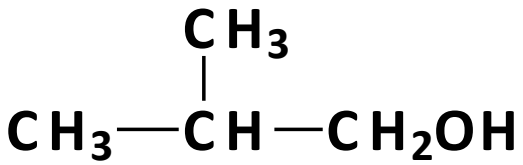
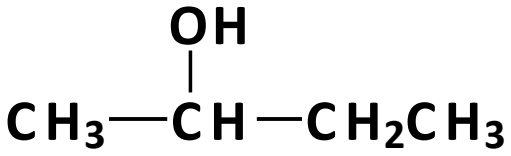


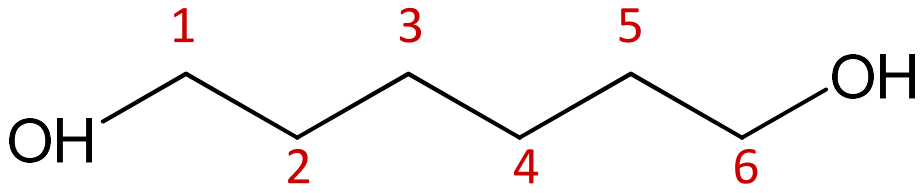
isobutyl alcohol
IUPAC: 2-methylpropan-1-ol



***sec*-butyl alcohol**
IUPAC: butan-2-ol

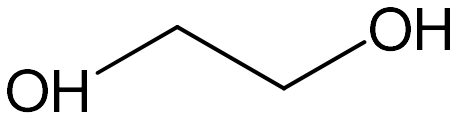
Naming polyalcohols

- Use -**diol, triol, tetraol**, etc. for alcohols bearing two, three, four, etc as suffix instead of -ol in polyalcohol compounds.

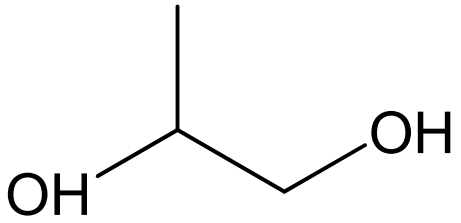


hexane-1,6-diol

- 1,2-diols (vicinal diol) are called **glycols**. Common names for glycols use the name of the alkene from which they were made.



IUPAC: ethane-1,2-diol
ethylene glycol

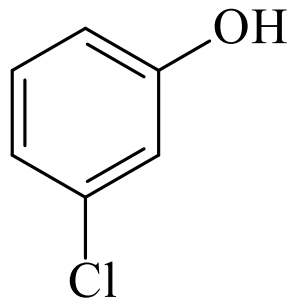


IUPAC: propane-1,2-diol
propylene glycol

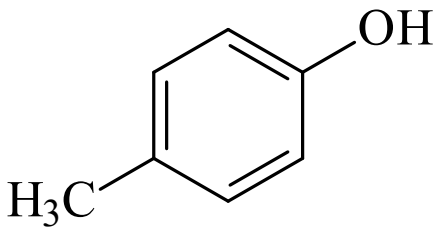
Phenol Nomenclature

Method

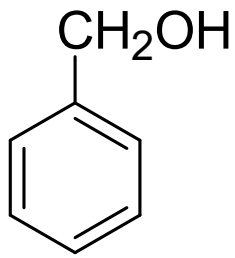
- —OH group is assumed to be on **carbon 1**.
- For common names of di-substituted phenols, use *ortho-* for 1,2; *meta-* for 1,3; and *para-* for 1,4.



3-chlorophenol
(meta-chlorophenol)



4-methylphenol
(para-methylphenol
Or Para-cresol)



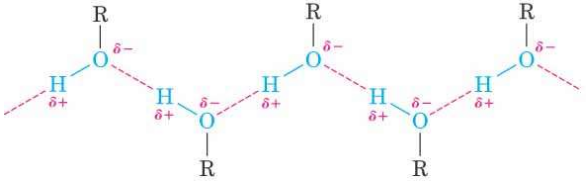
Phenylmethanol

- Use "phene" (the French name for benzene) as the parent hydrocarbon name, not benzene

➡ If it is substituent, called "**phenyl**"

Properties of Alcohols and Phenols

- Alcohols and phenols can form **Hydrogen Bonds**
  - **hold** the two molecules together
  - Alcohols and phenols have much **higher** boiling points than similar alkanes and alkyl halides
- **Small** alcohols are miscible in **water**, but solubility **decreases** as the size of the alkyl group increases.



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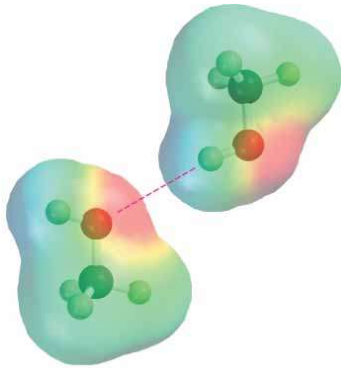

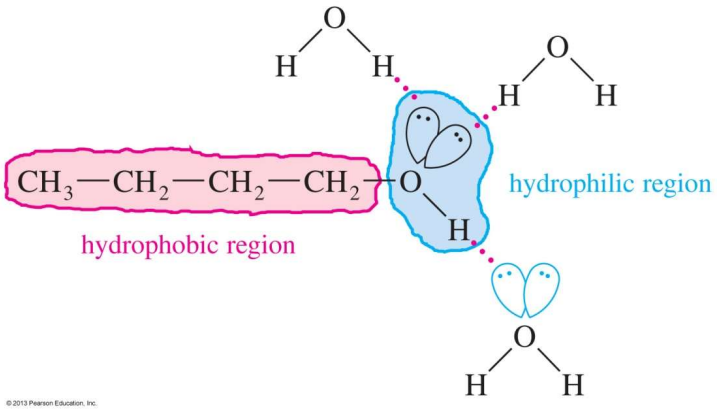

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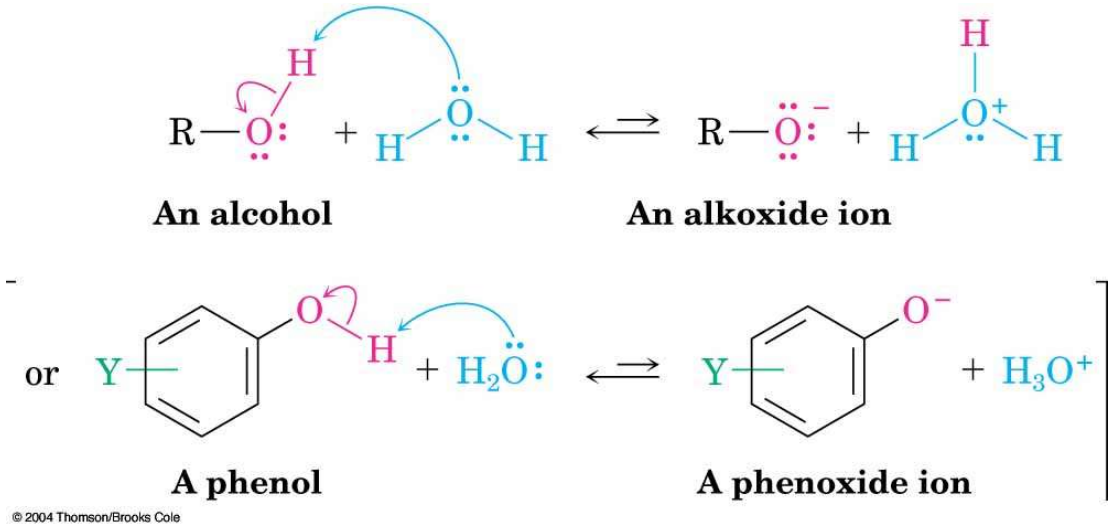
Acidity of alcohol and phenols

- They can **transfer** a proton to water to a very small extent
- Produces H_3O^+ and an **alkoxide ion**, **RO^-**, or a **phenoxide ion**, **ArO^-**



$$K_a = \frac{[H^+][RO^-]}{[ROH]}$$ and $pK_a = -\log K_a$

pK_a Values for Typical OH Compounds

- pK_a range of alcohols : 15.5–18.0 (water: 15.7)
- pK_a range of Phenols : around 10.0 (water: 15.7)

➡ Phenols is **weak acid**

TABLE 17.1 Acidity Constants of Some Alcohols and Phenols

Alcohol or phenol	pK_a
$(CH_3)_3COH$	18.00
CH_3CH_2OH	16.00
HOH (water)	(15.74)
CH_3OH	15.54
CF_3CH_2OH	12.43
p-Aminophenol	10.46
p-Methoxyphenol	10.21
p-Methylphenol	10.17
Phenol	9.89
p-Chlorophenol	9.38
p-Bromophenol	9.35
p-Nitrophenol	7.15
2,4,6-Trinitrophenol	0.60

Weaker acid

Stronger acid

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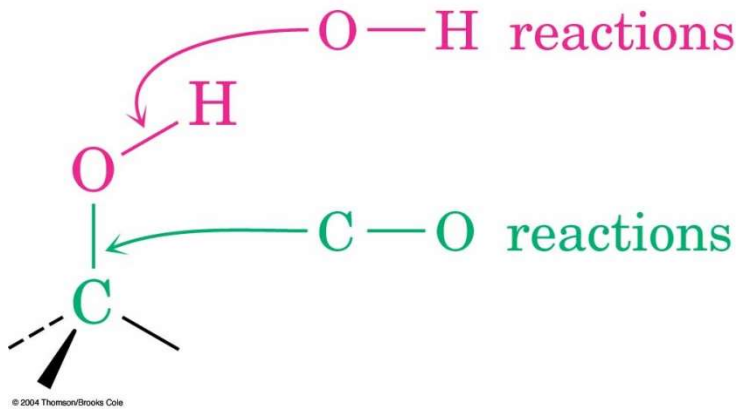
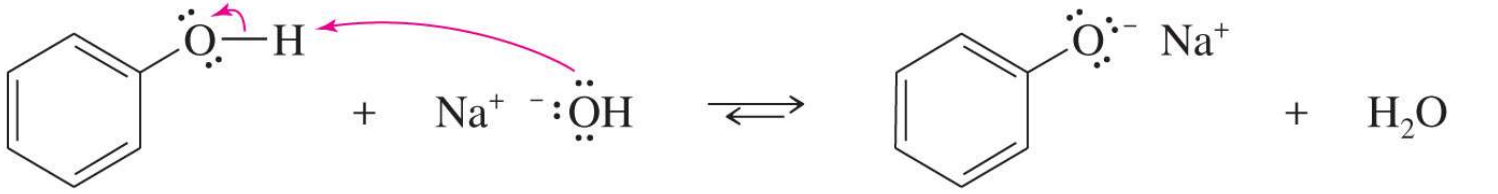
Reactions of Alcohols and phenols

- **Two** general classes of reaction
  - At the carbon of the **C–O** bond
  - At the proton of the **O–H** bond



- Because phenols are weak acids (reacted with strong bases, reaction at proton of O-H bond is easier.



phenol, $pK_a = 10.0$ sodium phenoxide $pK_a = 15.7$

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Example

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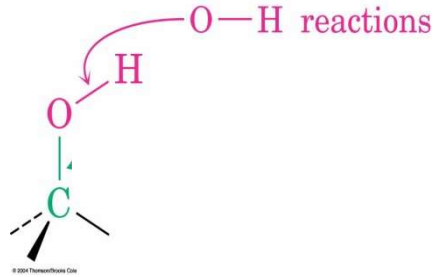
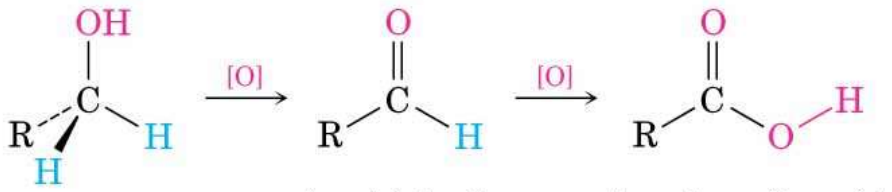


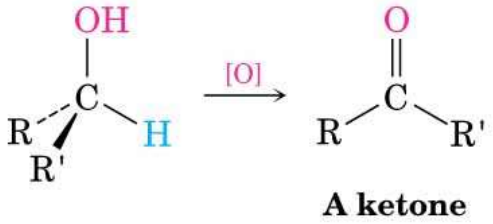
Reactions of alcohols (not phenols)

Oxidation of Alcohols: Can be accomplished by inorganic reagents, such as $KMnO_4$, CrO_3, and $Na_2Cr_2O_7$

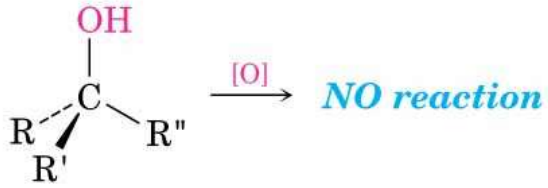
Primary alcohol



Secondary alcohol



Tertiary alcohol



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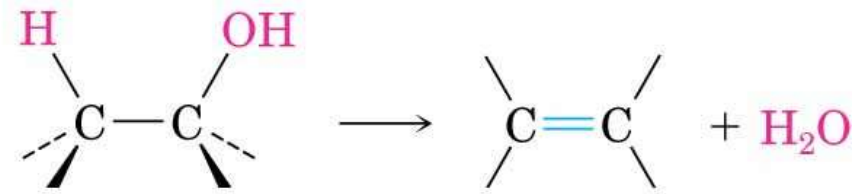
Give the product formed from the reaction of each of the following compounds with chromic acid:

a. 3-pentanol **b.** 1-pentanol **c.** cyclohexanol **d.** benzyl alcohol

Reactions of alcohols (not phenols)

A dehydration reaction



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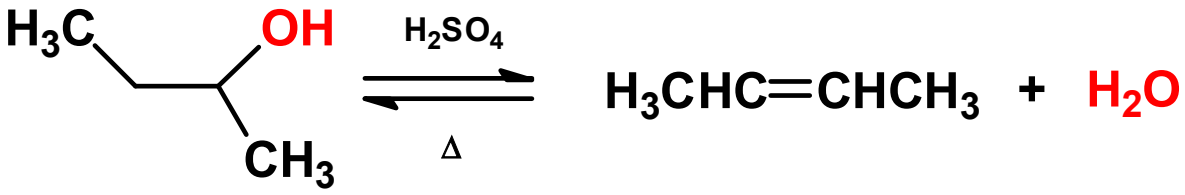
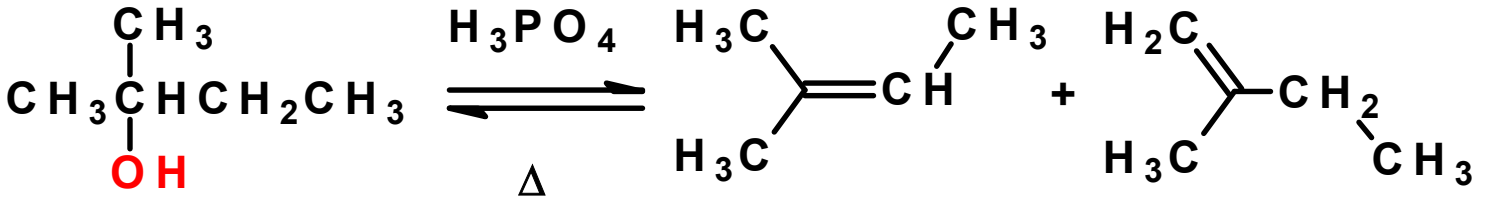
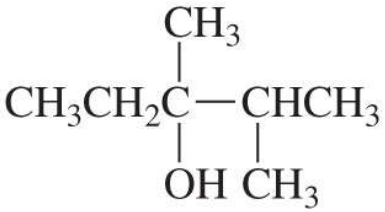
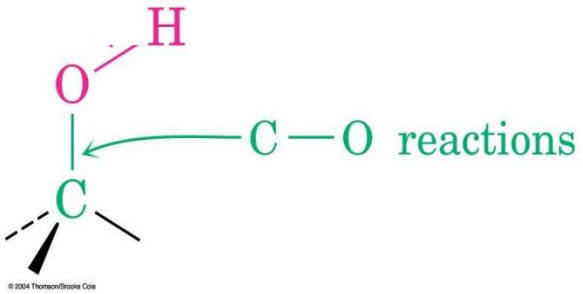
According to **Zaixep's rule**





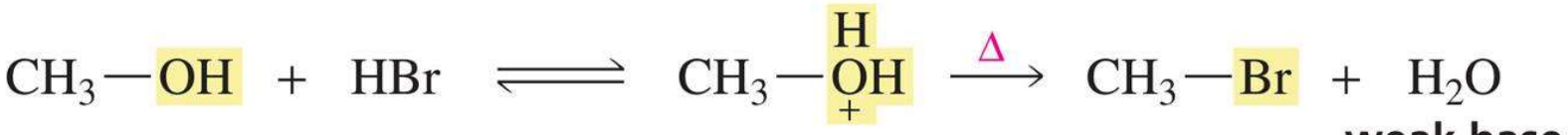
Give the major product formed when each of the following alcohols is heated in the presence of H_2SO_4:

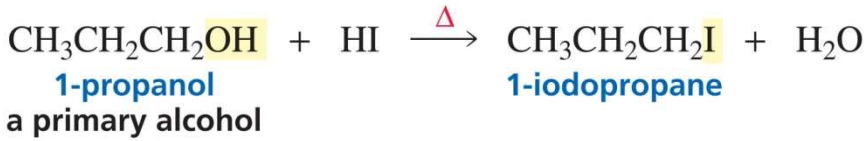


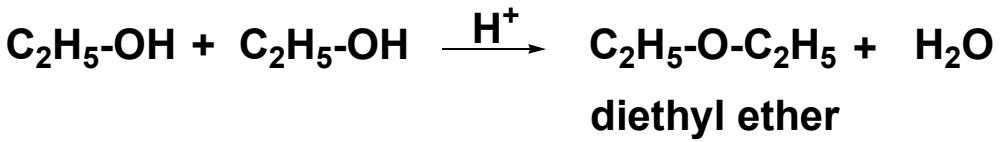


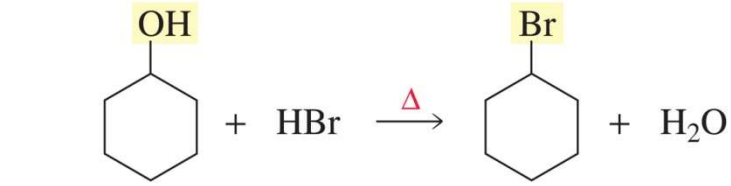
Reactions of alcohols (not phenols)

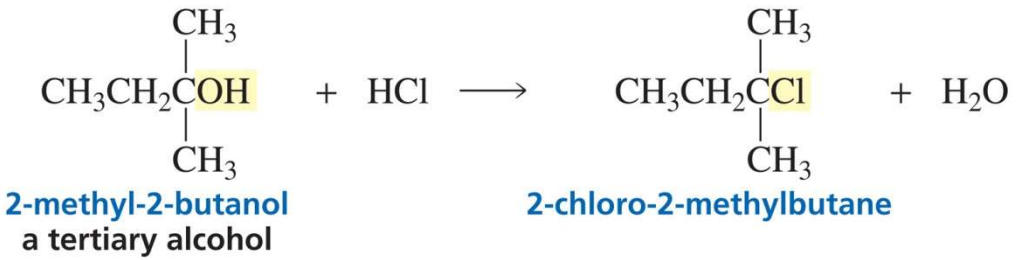
- Substitution Reactions: *OH group of alcohols can be substituted by* **halogen group** or **alcohol** with acid catalyst











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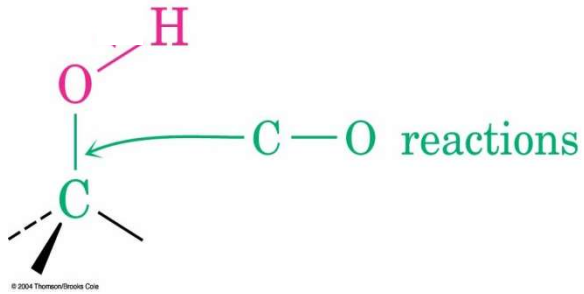
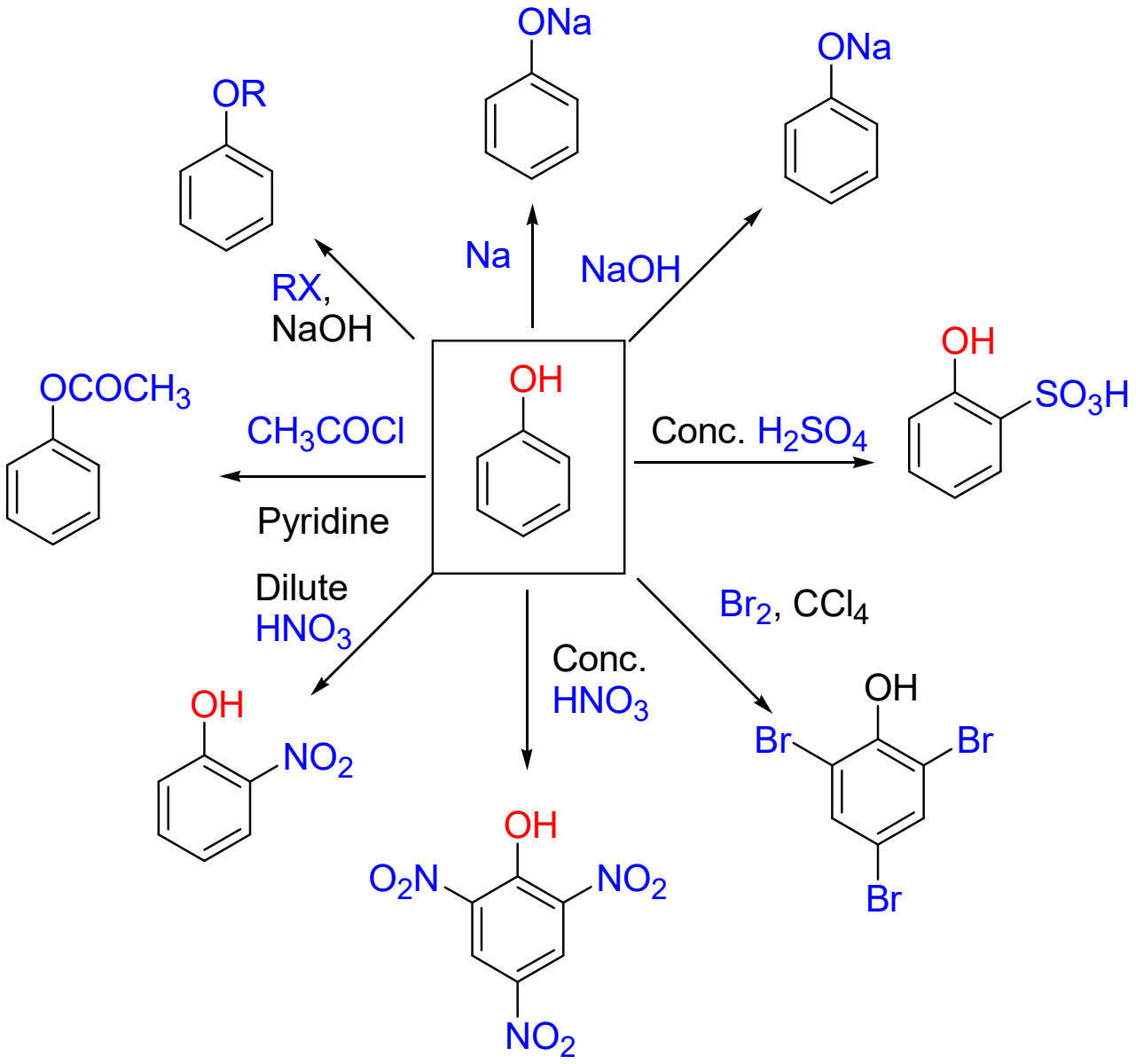
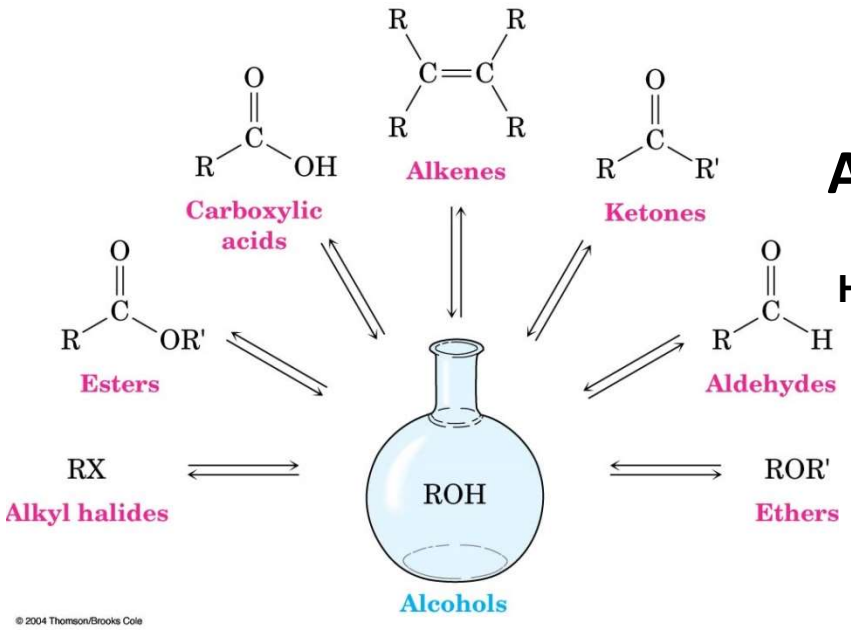


Reactions of phenols



Preparation of alcohols



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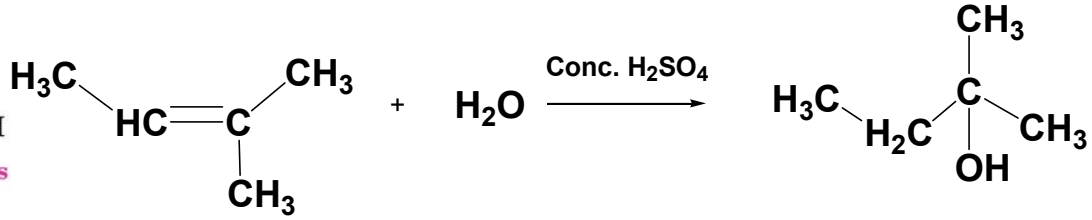
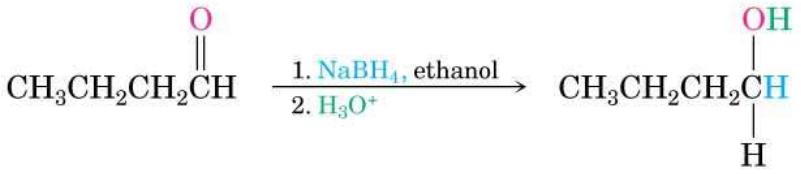
Addition of water

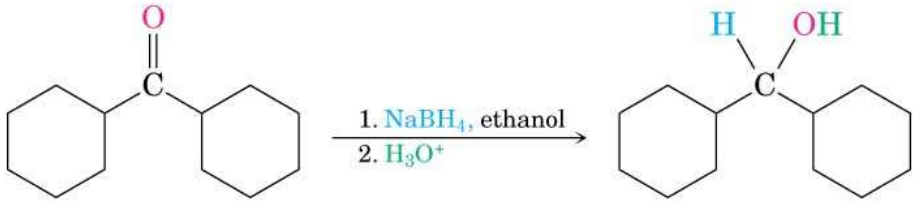


Aldehyde reduction



Butanal — **1-Butanol (85%) (a 1° alcohol)**

Ketone reduction



Dicyclohexyl ketone — **Dicyclohexylmethanol (88%) (a 2° alcohol)**

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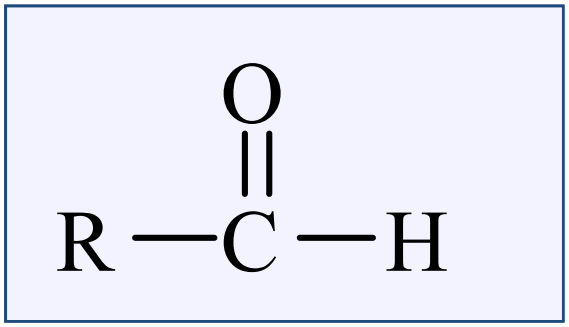
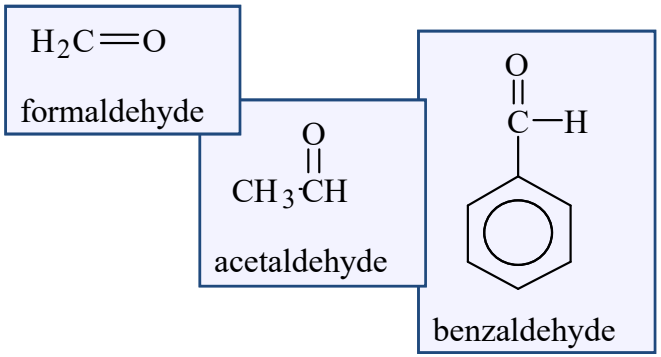
2. Aldehydes and Ketones (Carbonyl Group)

Carbonyl Group C=O: Present in **aldehydes** and **ketones**

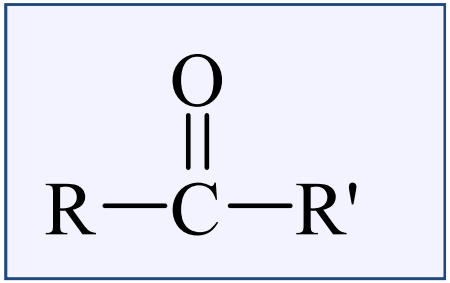
- Aldehydes have abbreviated formulas RCHO Containing at least one H connected to the C



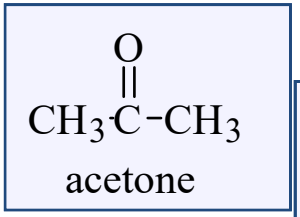
Aldehydes

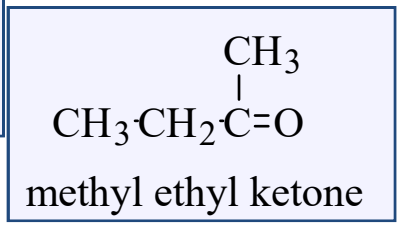


- Ketones have abbreviated formulas RCOR' and Carbonyl C is connected to two alkyl groups.



Ketones

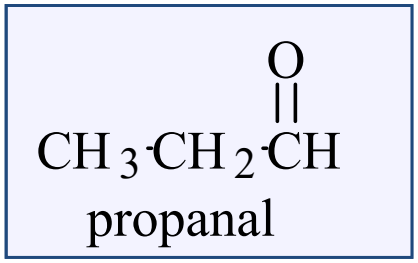


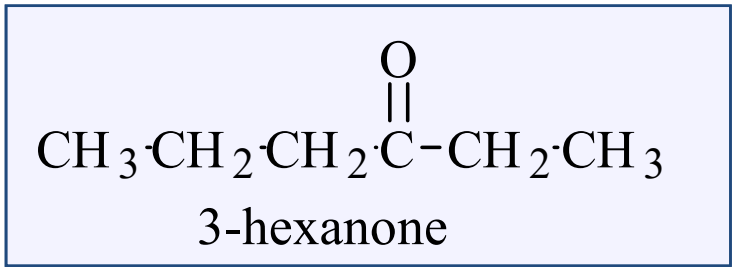


Nomenclature of aldehydes and ketones (IUPAC)

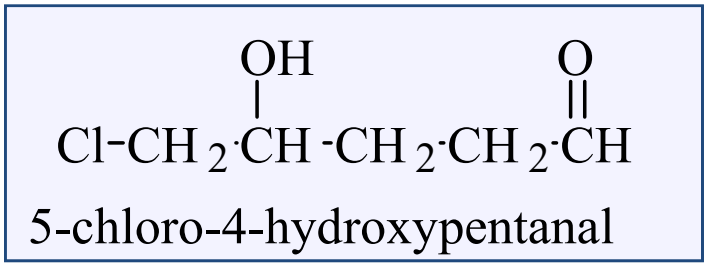
IUPAC Name:

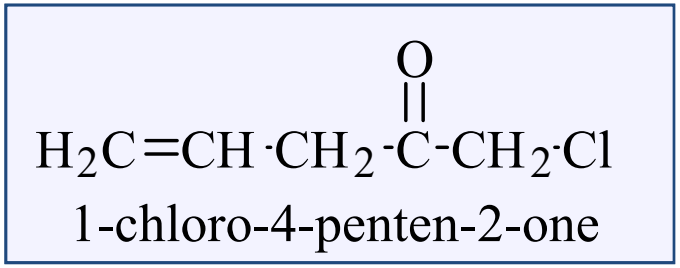
- Suffix is "-al" for the aldehydes
- Suffix is "-one" for the ketones
- indicates position of ketone





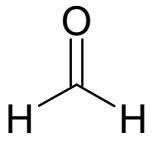
- An Aldehyde or Ketone takes precedence over any previously considered group



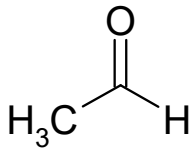


Common names of aldehydes

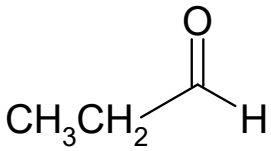
Using "**aldehyde**"



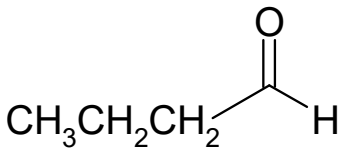
Methanl
(formaldehyde)



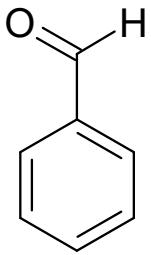
ethanal
(acetaldehyde)



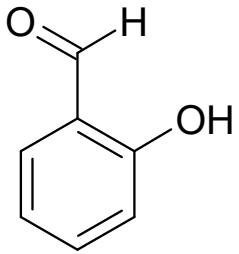
propanal
(propionaldehyde)



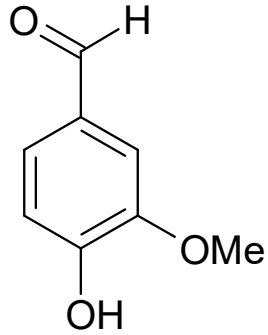
butanal
(n-butyraldehyde)



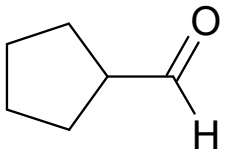
benzaldehyde



salicylaldehyde
(2-hydroxybenzenecarbaldehyde)



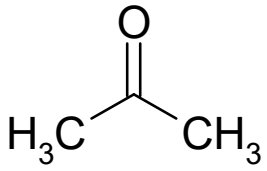
Vanillin



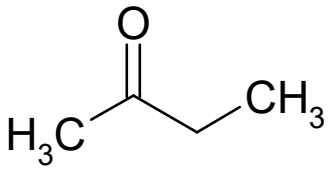
cyclopentanecarbaldehyde

Common names of Ketones

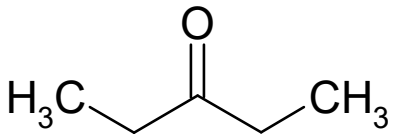
- Named as **alkyl** attachments to **—C=O**.
- Use **Greek letters** instead of numbers.
- **Historical** Common Names



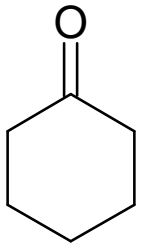
propanone (acetone)



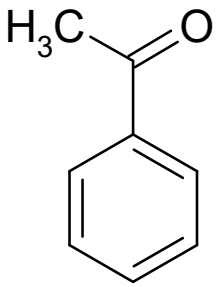
2-butanone (ethyl methyl ketone)



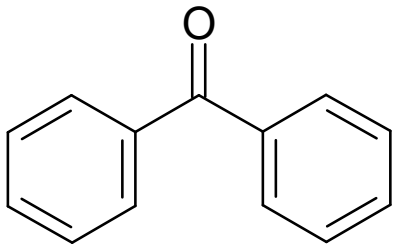
3-pentanone (diethyl ketone)



cyclohexanone

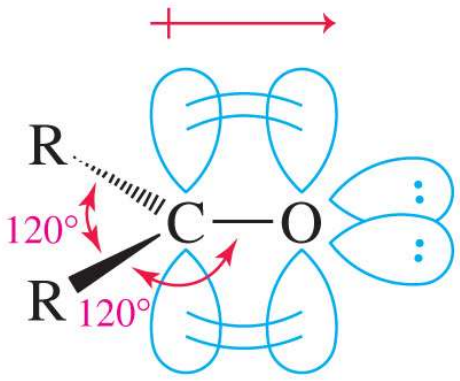


acetophenone (methyl phenyl ketone)



benzophenone (diphenyl ketone)

Carbonyl structure



	length	*energy*
ketone C═O bond	1.23 Å	745 kJ/mol (178 kcal/mol)
alkene C═C bond	1.34 Å	611 kJ/mol (146 kcal/mol)

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- Carbon is sp^2 hybridized.
- C=O bond is shorter, stronger, and more polar than C=C bond in alkenes.

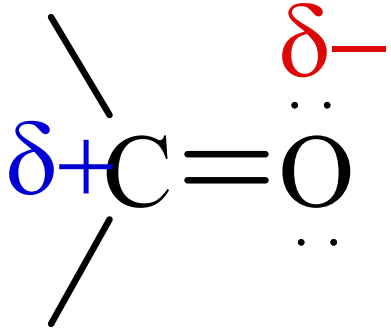
→ C=O is more stable than C=C

Physical Properties

- Carbonyl compounds **cannot** form H bonding with each other Because there is NOT an H connected to a F, N, O

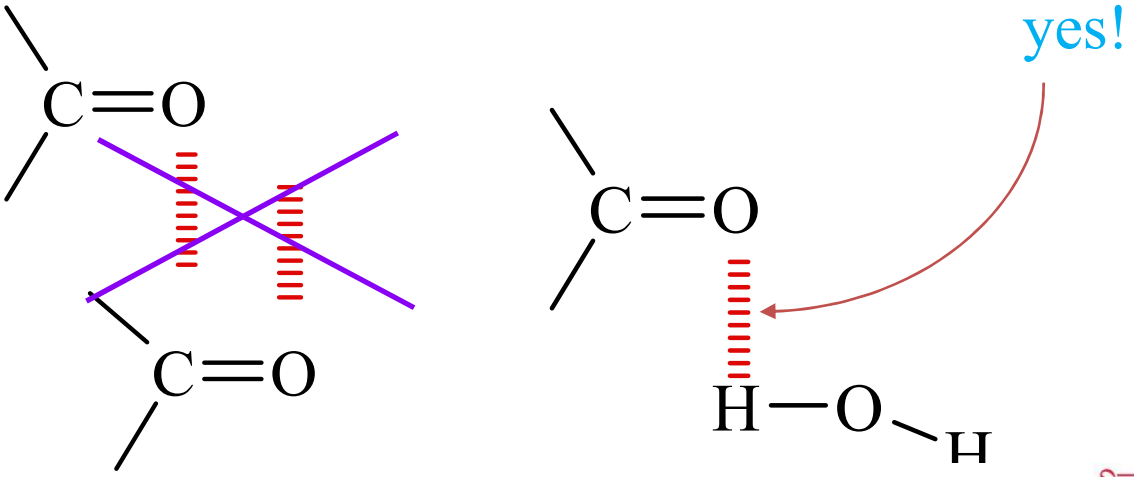
- Aldehydes and Ketones are **POLAR** molecules and form dipole interactions

- Aldehydes and Ketones give **higher** boiling and melting points than hydrocarbon which have the same carbon number

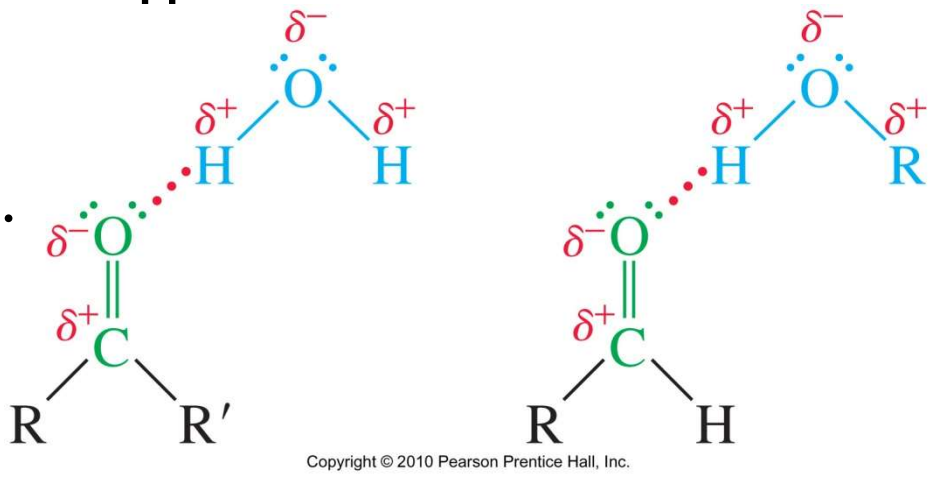


Physical Properties

- Aldehydes and Ketones
  - **can** form H bonds with **water**!
  - **solubility** in water is about the same as **alcohols**.
    Acetone and acetaldehyde are **miscible** in water.



- **Good** solvent for alcohols.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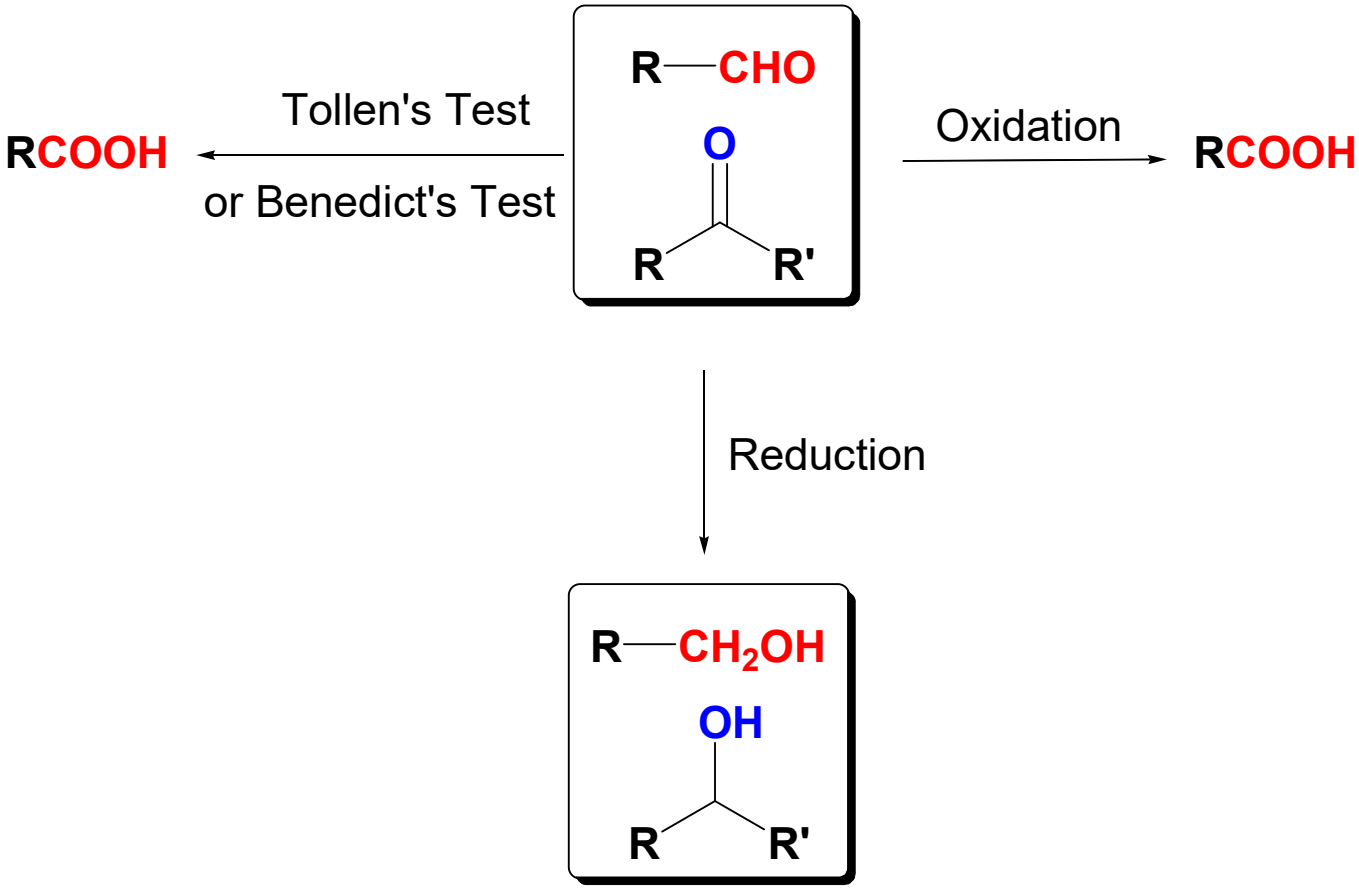
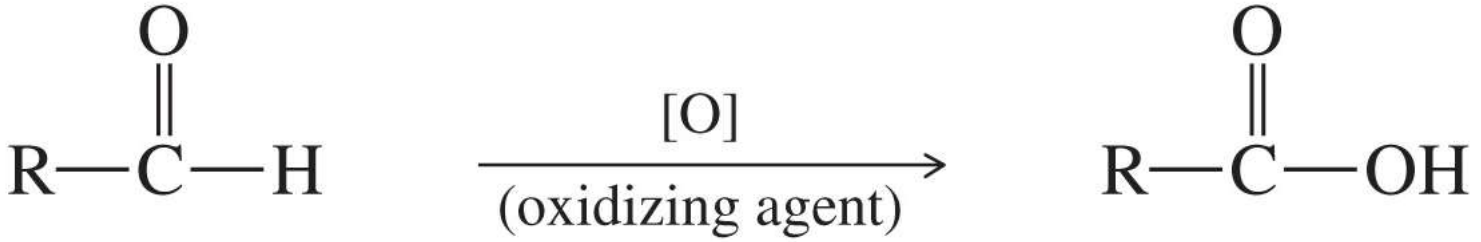
Chemical properties

1. Oxidation
   - Tollens Test
   - Benedicts Test
2. Reduction
   - Hydrogen addition
   - $NaBH_4$ reagent

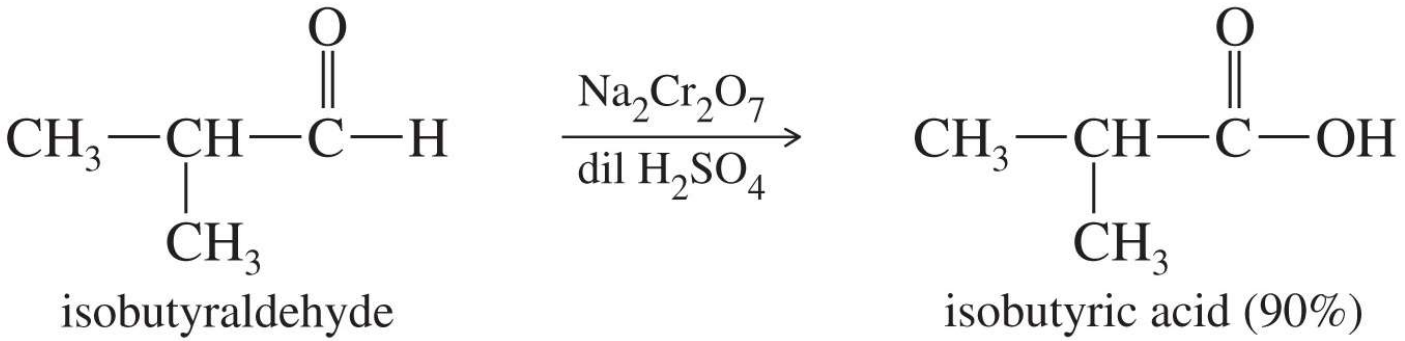


Oxidation by common reagents

Only aldehyde is oxidized

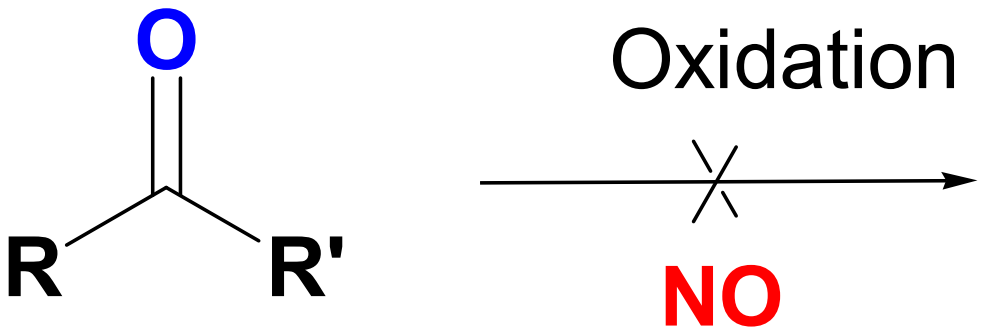


Examples



isobutyraldehyde

isobutyric acid (90%)



Tollen's Test

The **Silver Mirror** Test: Oxidation of Aldehydes

- Ag^+ ion in aq. ammonia
- **NO** reaction with KETONES

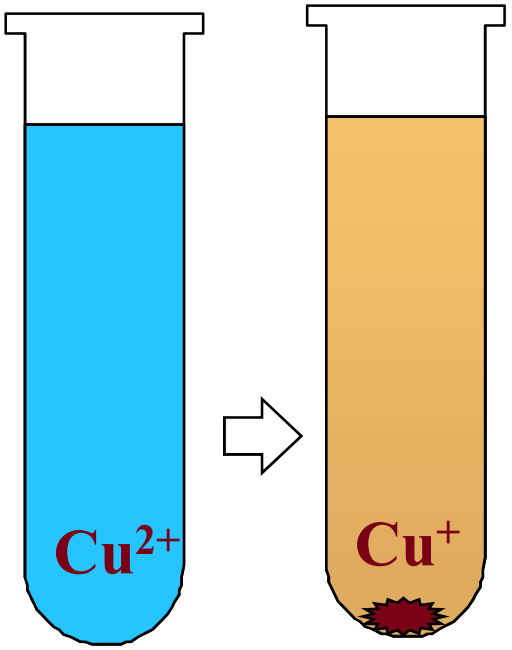
$$Ag(NH_3)_2^+ + \text{aldehyde} \longrightarrow \text{Silver Mirror}$$

$$Ag^+ + 2\,NH_3 \rightarrow Ag(NH_3)_2^+$$

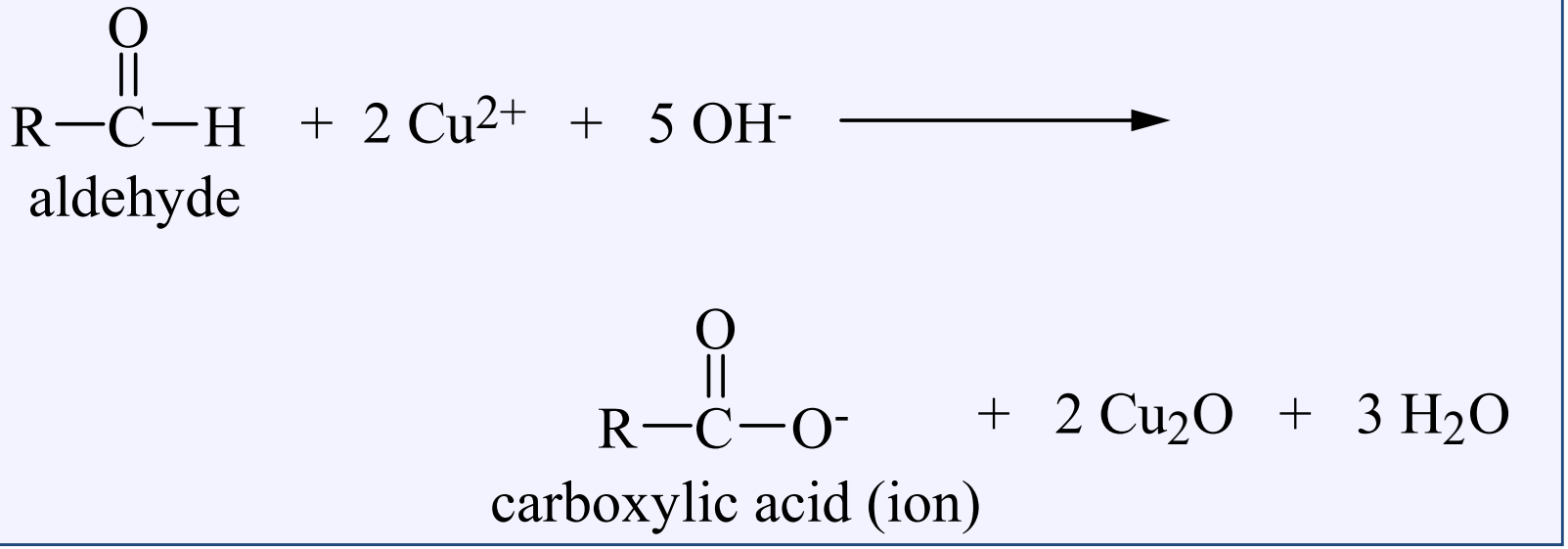
$$Ag(NH_3)_2^+ + RCHO \rightarrow Ag^o + RCOO^- + 4NH_3$$

Benedict's Test

- Oxidation of Aldehydes
  - Cu^{2+} ion, aqueous
  - **NO** reaction with KETONES



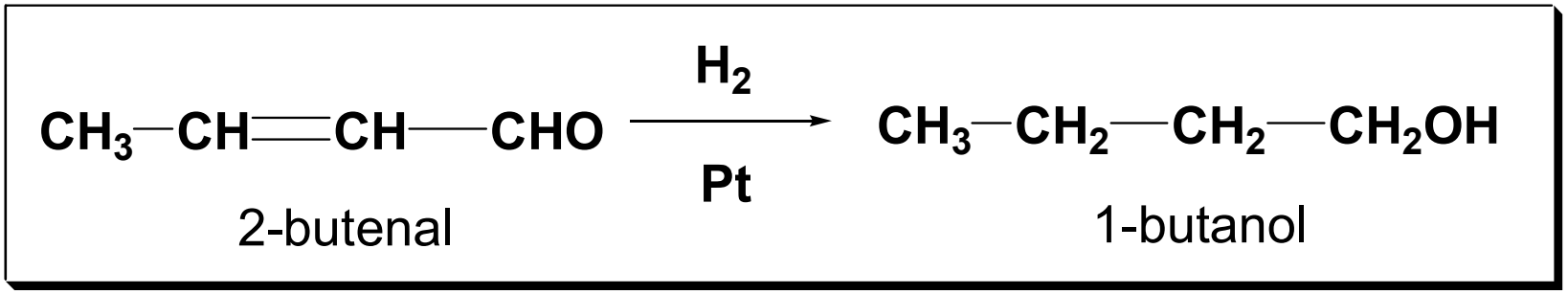
Cu^{2+} + aldehyde ⇨ $Cu^{+}_{(oxide)}$ + acid

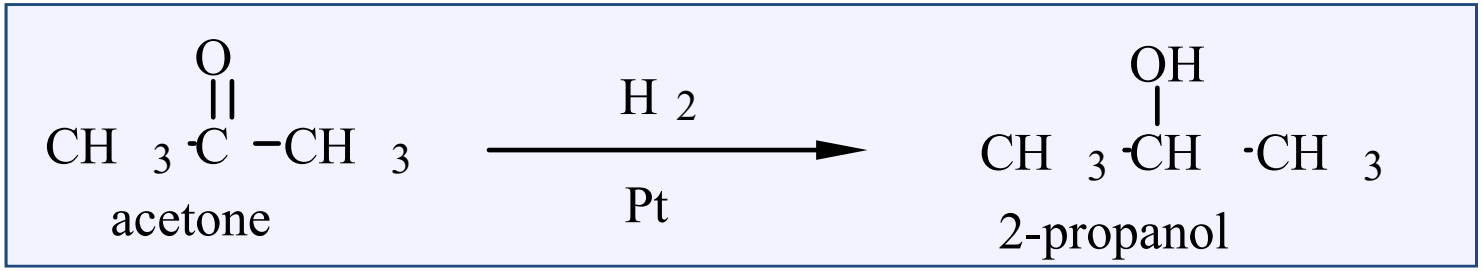


Addition of H_2 (reduction)

Reduction to Alcohols:

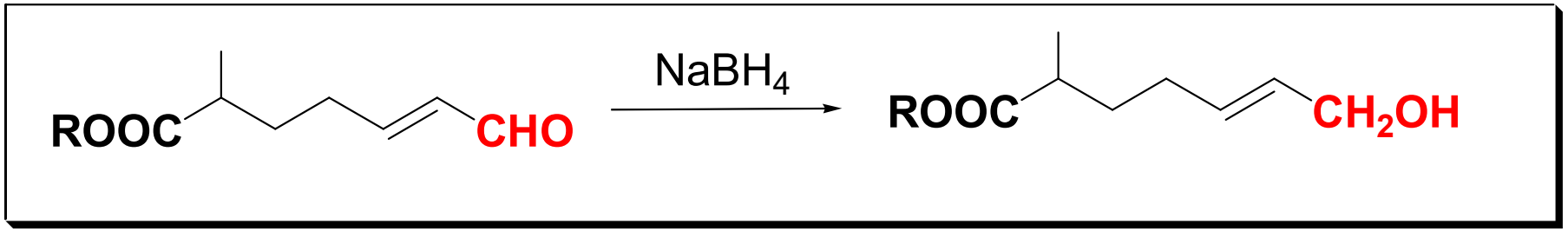
- **Both** aldehyde and ketone are reduced by Hydrogen gas and a catalyst (Ni, Pd, Pt)
- **Similar** to alkene to alkane reduction
- Aldehyde → **primary** alcohol
- Ketone → **second** alcohol

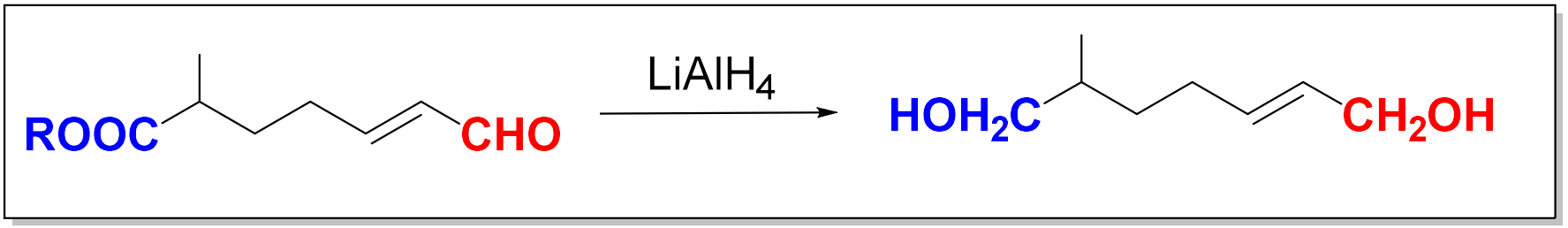




Reduction using $NaBH_4$ or $LiAlH_4$

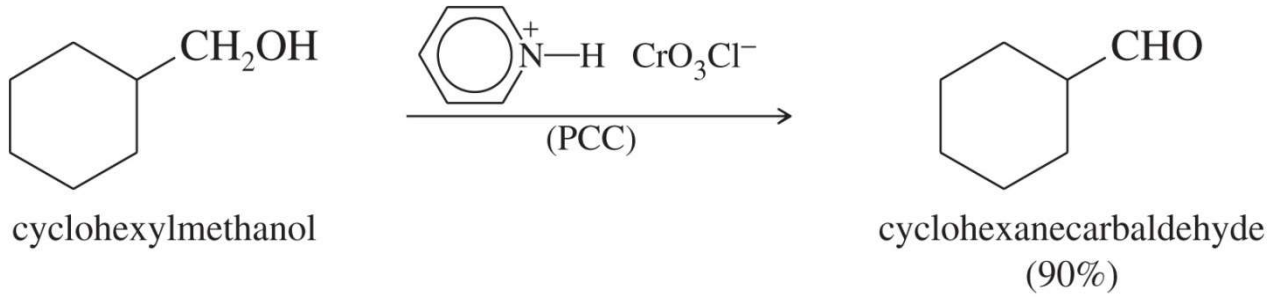
- $NaBH_4$ can reduce ketones and aldehydes, but **NOT** esters, carboxylic acids, acyl chlorides, or amides.
- $LiAlH_4$ can reduce **ANY** carbonyl because it is a very strong reducing agent.



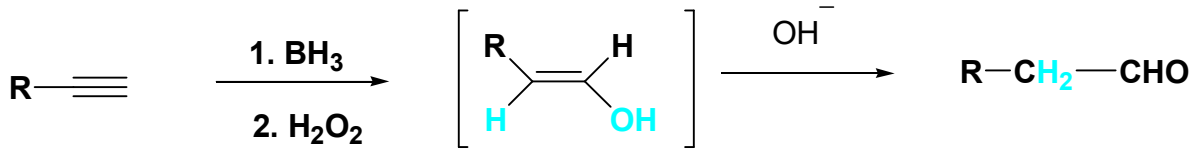


Preparation of aldehyde

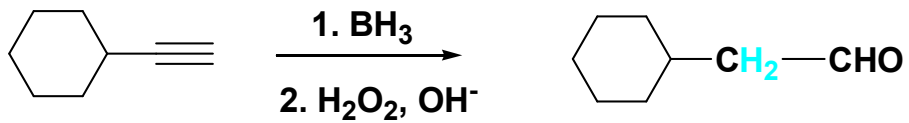
- **Oxidation of Primary Alcohols** to Aldehydes: Pyridinium chlorochromate (**PCC**) is selectively used to oxidize primary alcohols to **aldehydes**.



- **Hydroboration–oxidation** of an alkyne gives anti-**Markovnikov** addition of water across the triple bond.

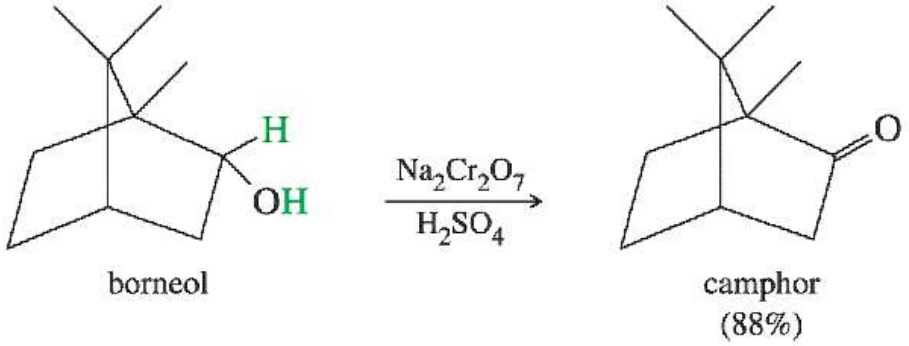


Example

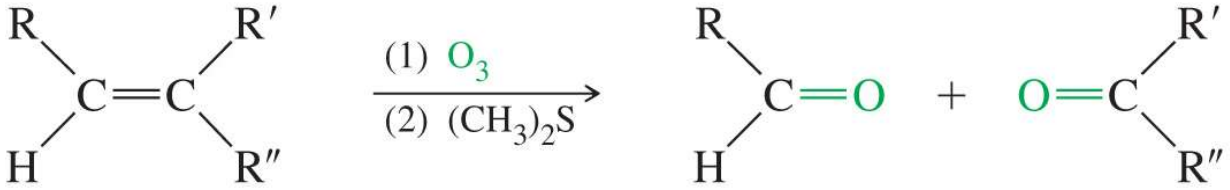


Preparation of Ketones

- **Secondary** alcohols are readily oxidized to **ketones** with sodium dichromate ($Na_2Cr_2O_7$) in sulfuric acid or by potassium permanganate ($KMnO_4$).

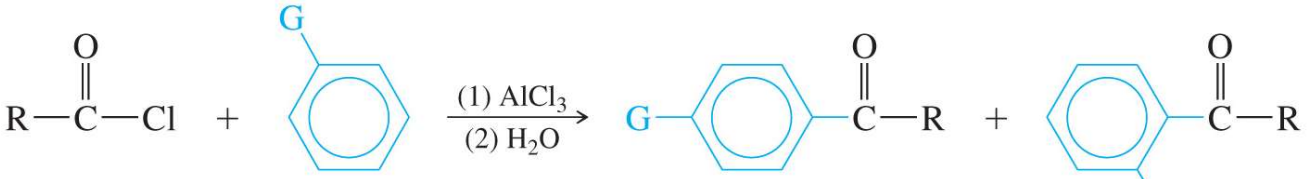


- The double bond is oxidatively cleaved by ozone followed by reduction. **Ketones** and **aldehydes** can be isolated as products.

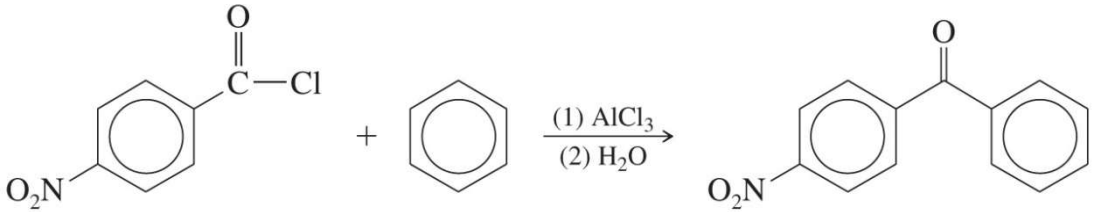


Preparation of Ketones

- Reaction between an **acyl halide** and an **aromatic** ring will produce a ketone.



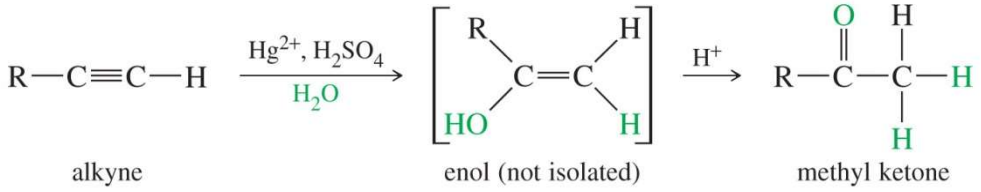
R is alkyl or aryl; G is hydrogen, an activating group, or a halogen.



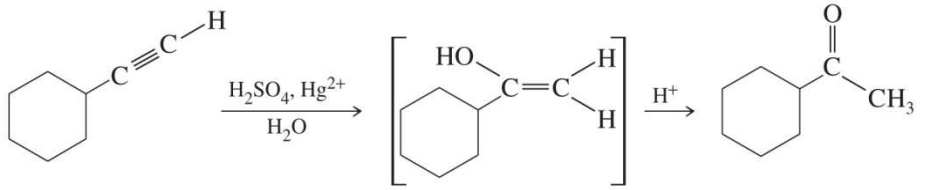
p-nitrobenzoyl chloride

p-nitrobenzophenone (90%)

- The initial product of **Markovnikov** hydration is an **enol**, which quickly tautomerizes to its keto form.



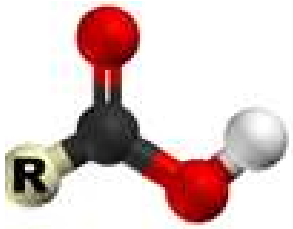
alkyne enol (not isolated) methyl ketone

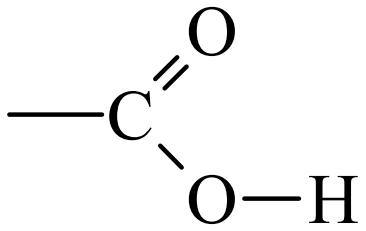


ethynylcyclohexane enol cyclohexyl methyl ketone (90%)

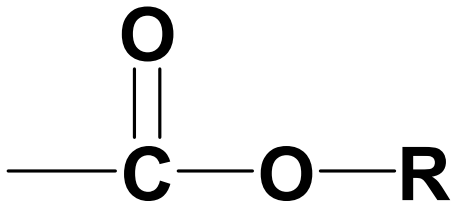
3. Carboxylic acid and esters

- **Carboxylic acids** are strong organic acids which contain the **carboxyl group (-COOH, $-CO_2H$)**





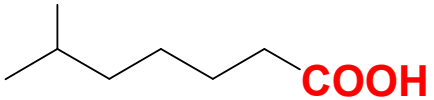
- **Esters** are derivatives of organic acid which contain the group **-COOR**



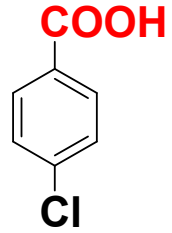
3.1. Carboxylic acid

- Carboxylic acids are classified as **aliphatic** or **aromatic** depending on whether R or an Ar is attached to the carboxylic group

  R-COOH or **Ar-COOH**



Aliphatic acid



Aromatic acid

Nomenclature

Formula	IUPAC alkan -oic acid	Common prefix – ic acid
HCOOH	methanoic acid	formic acid
CH_3COOH	ethanoic acid	acetic acid
CH_3CH_2COOH	propanoic acid	propionic acid
$CH_3CH_2CH_2COOH$	butanoic acid	butyric acid

Nomenclature

Naming Rules

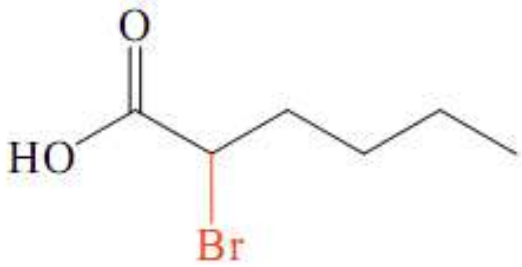
- Identify the longest chain
- (IUPAC) Number carboxyl carbon as 1
- (Common) Assign α, β, γ, δ to carbon atoms adjacent to carboxyl carbon

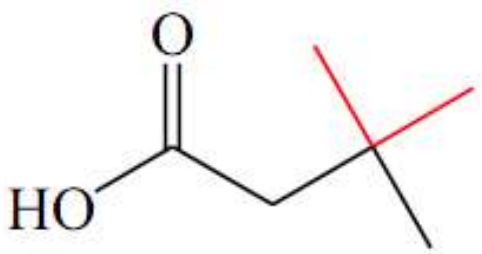
5 4 3 2 1

C—C—C—C—C=O

δ γ β α ← used in common names

Examples:





IUPAC: 2- bromohexanoic acid

Common: α- bromohexanoic acid

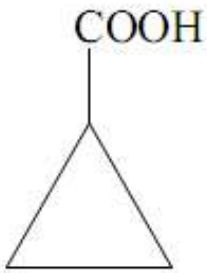
3,3-dimethylbutanoic acid

β,β-dimethylbutyric acid

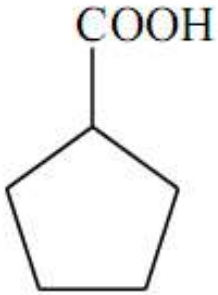
Nomenclature

Naming Cyclic Carboxylic Acids

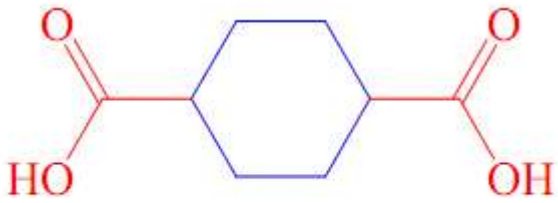
- Cyclic compounds containing one or more COOH groups attached to the ring are named by identifying the **name of the ring** followed by the word **carboxylic acid** or **dicarboxylic acids** etc.



Cyclopropane carboxylic acid

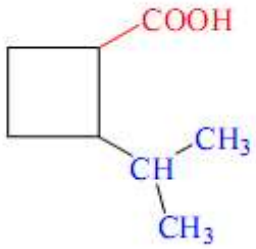


Cyclopentanecarboxylic acid

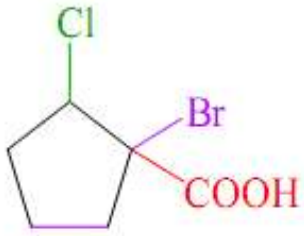


1,4-Cyclohexanedicarboxylic acid

- The **carbon atom** bearing the carboxylic group is numbered **1** and the substituents are numbered relative to it.



2-Isopropylcyclobutane carboxylic acids

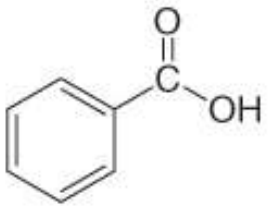


1-Bromo-2-chlorocyclopentane carboxylic acids

Nomenclature

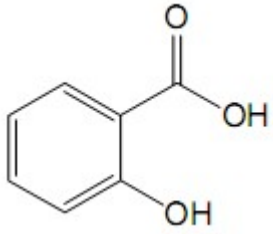
Naming Aromatic Carboxylic Acids

- The **simplest** aromatic carboxylic acid is benzoic acid.
- Substituted benzoic acids are named with **benzoic acid** as the parent name.
- Derivatives are named using **numbers** to show the location of substituents relative to the carboxyl group.
- The ring carbon attached to the carboxyl group is the **#1** position.



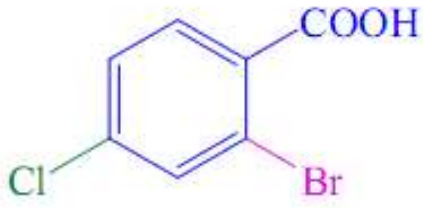
Benzoic acid

Benzene carboxylic acid



Salicylic acid

2-Hydroxybenzoic acid

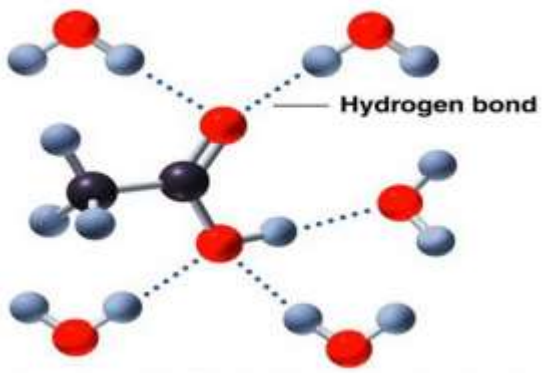


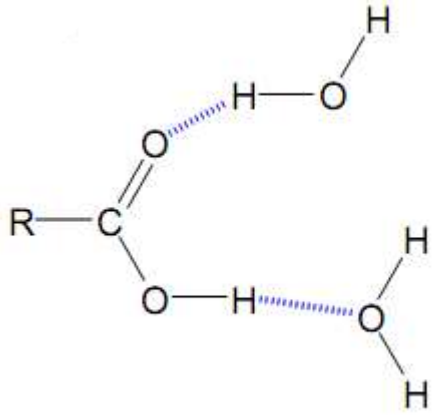
2-Bromo-4-chloro benzoic acid

Physical Properties of Carboxylic Acids

Solubility

- The carboxylic acid are **highly polar** organic compounds.
- This **polarity** results from the presence of a strongly polarized carbonyl (C=O) group and hydroxyl (O-H) group.





Water Solubility:

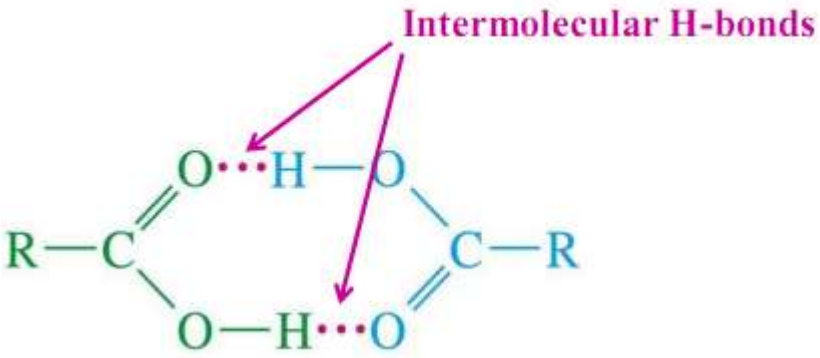
Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

- As the **number** of carbons in a carboxylic acid series becomes **greater**, the **solubility** in water **decreases**.
- **Aromatic** carboxylic acids are **insoluble** in water.

Physical Properties of Carboxylic Acids

Boiling Point

- Carboxylic acids are **polar** compounds and form very strong intermolecular **hydrogen** bonds to form a **dimer**.



Boiling Point:

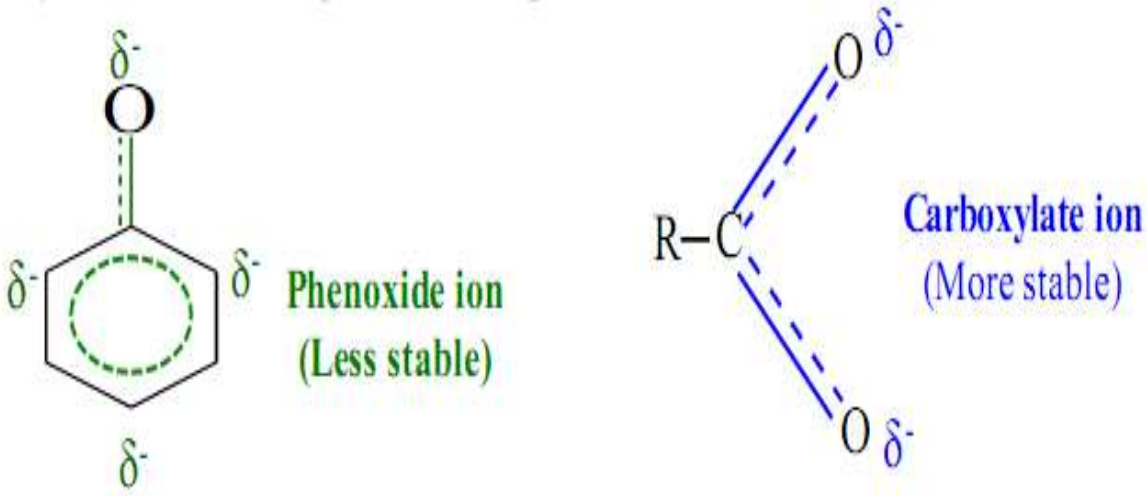
Carboxylic acid
Alcohols
Aldehydes/Ketones
Ethers
Alkanes

- As the number of carbons in a carboxylic acid series becomes **greater**, the boiling point **increases**.

Chemistry Properties of Carboxylic Acids

Acidity and Acid Strength

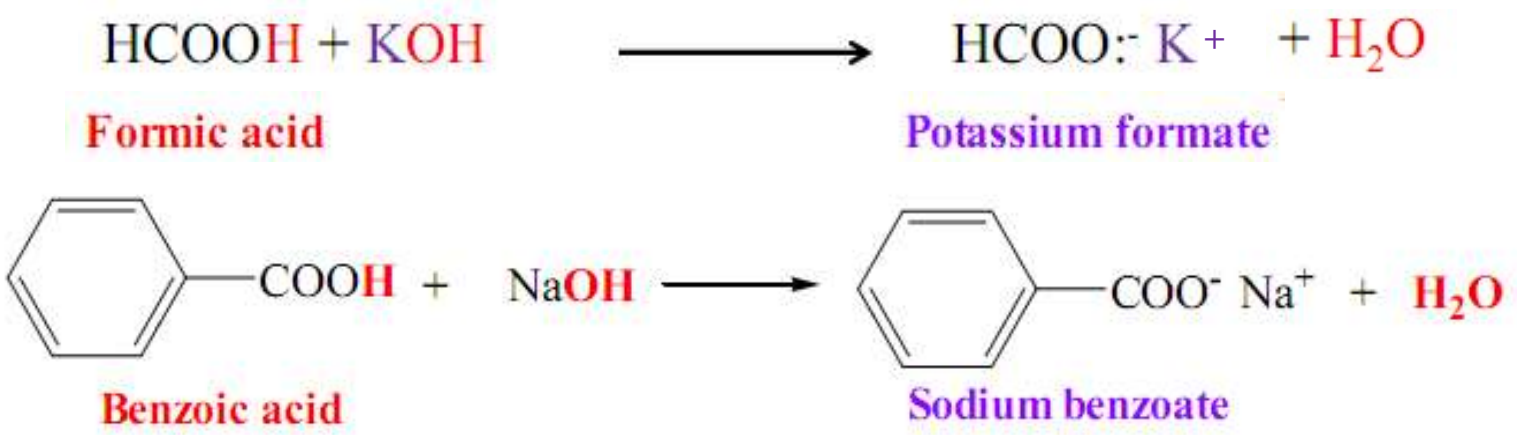
- The most important chemical property of carboxylic acids chemistry is their **acidic nature**.
- The mineral acids (HCl, HBr, HI, H_2SO_4, H_3PO_4) are defined as "strong acids" because they undergo complete dissociation.
- Carboxylic acids are strong organic acids , they are much more acidic **than alcohols**.
- Carboxylic acids are stronger acids than **phenols**.



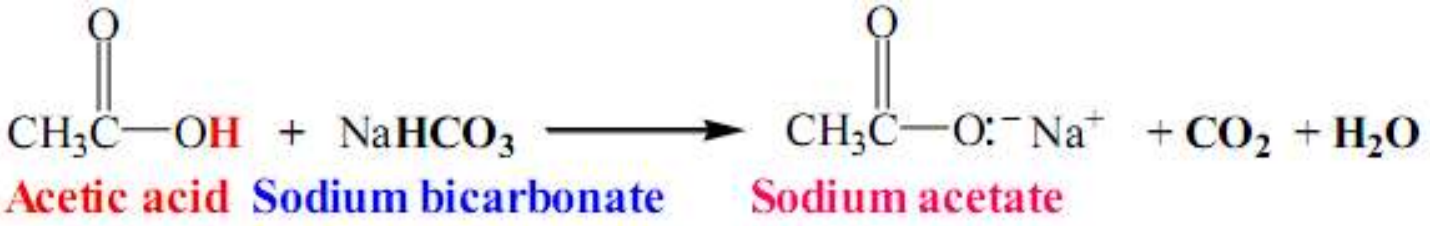
Chemistry Properties of Carboxylic Acids

Reaction with Bases : Salt formation and The carboxyl hydrogen is replaced by metal ion, M^+

- **With strong base:**



- **With weak base**

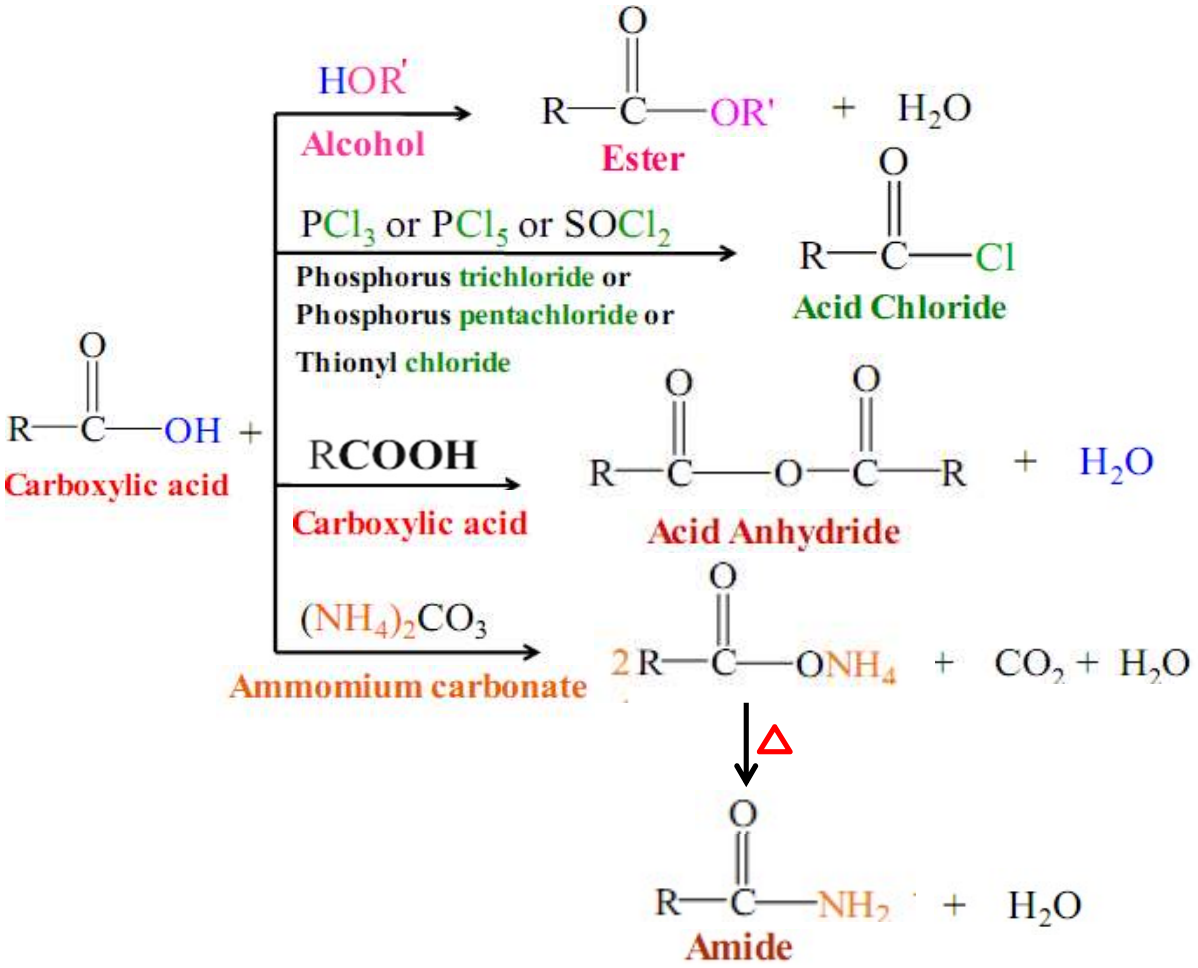


- Weaker acids like **phenols** react only with strong bases like (NaOH or KOH) and will not react with $NaHCO_3$

Chemistry Properties of Carboxylic Acids

Reaction with reagents (Nucleophiles) to form acid derivatives:

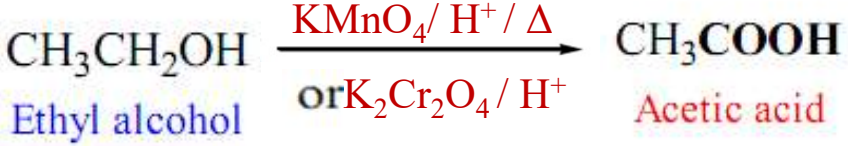
- When the **OH** of a carboxylic acid is replaced by a **nucleophile (:Nu)**, a **carboxylic acid derivative** is produced.

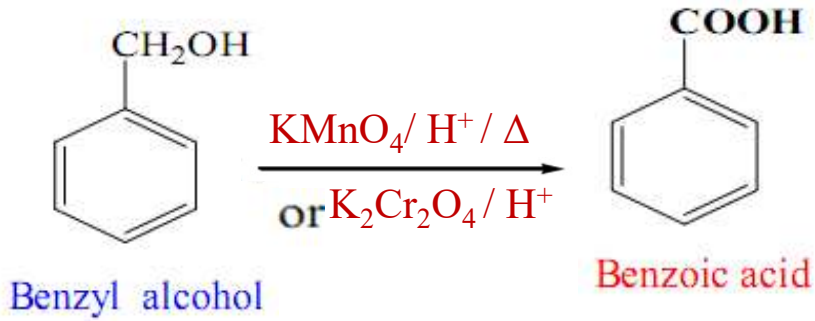


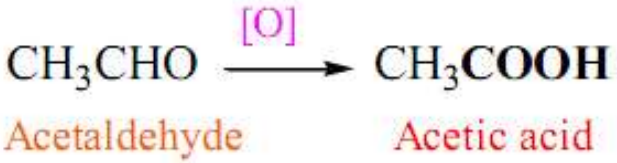
Preparation of Carboxylic Acids

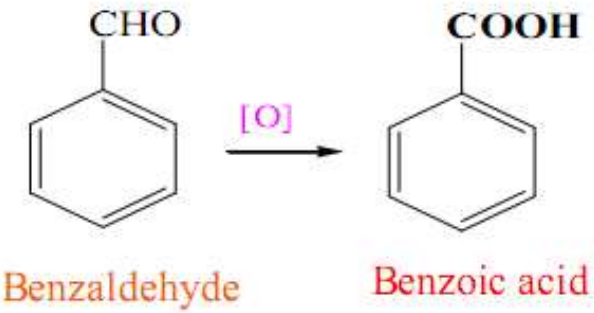
Oxidation

- Oxidation **of primary** alcohols and **aldehydes**

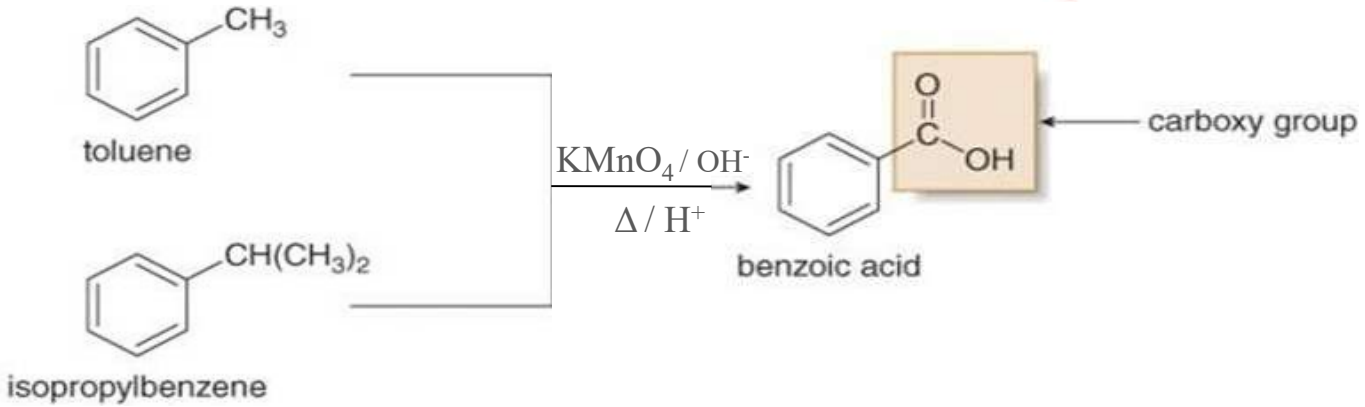








Oxidation of Alkylbenzene

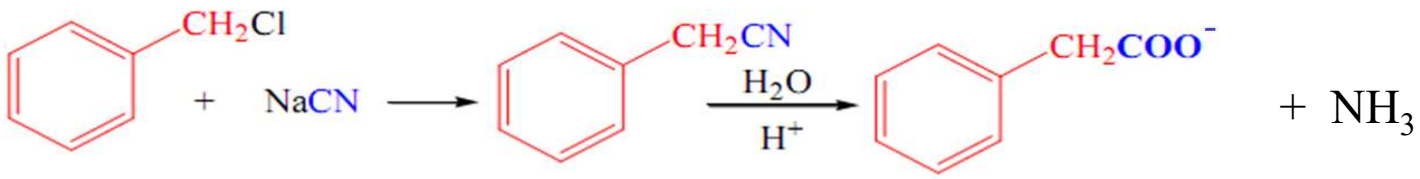


Preparation of Carboxylic Acids

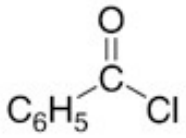
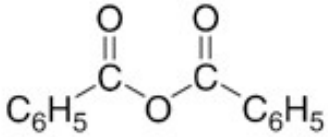
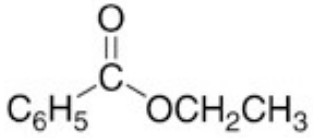
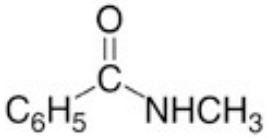
Hydrolysis of Nitriles:

Nitriles: $RC{\equiv}N$ or $ArC{\equiv}N$

- They are prepared by reacting a 1° or 2° alkyl halide with **cyanide salt**.
- Acid **hydrolysis** of a nitriles yields a carboxylic acids.



Derivatives of Carboxylic acids

Compound	Name ending	Example	Name
acid chloride	**-yl chloride** or **-carbonyl chloride**		benzoyl chloride
anhydride	**anhydride**		benzoic anhydride
ester	**-ate**		ethyl benzoate
amide	**-amide**		*N*-methylbenzamide

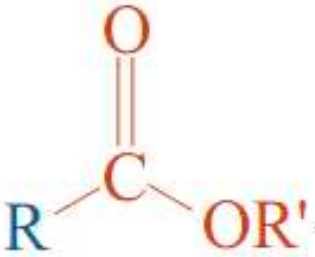
3.2 Esters

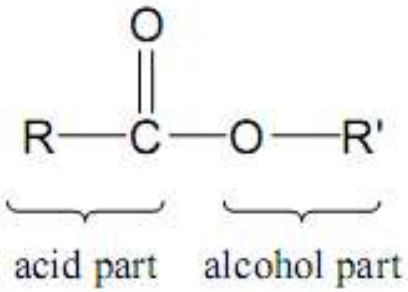
Nomenclature

- the functional derivatives' names are **derived** from the **common** or **IUPAC** names of the corresponding carboxylic acids.

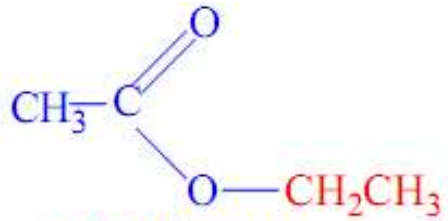
- Naming Ester: Change **–ic acid** to **–ate** preceded by the alkyl is derived from the alcohol, R'OH.

alkyl alkanoate

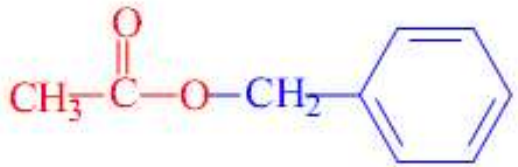




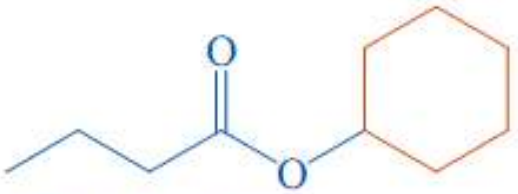
Examples:



Ethylethanoate



Benzyl ethanoate

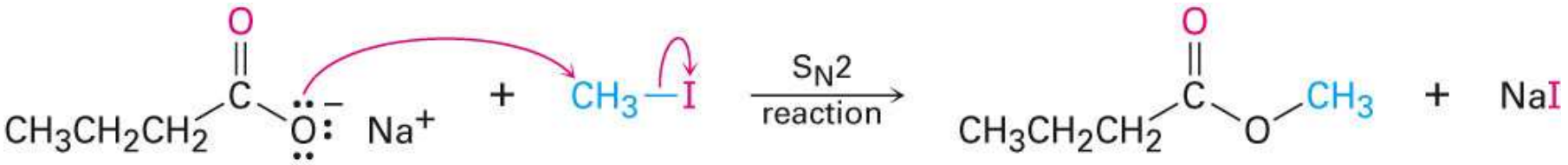


Cyclohexyl butanoate

Preparation of Esters

Conversion of Carboxylic Acids into Esters

Methods include reaction of a carboxylate anion with a **primary** alkyl halide



Sodium butanoate **Methyl butanoate (97%)**

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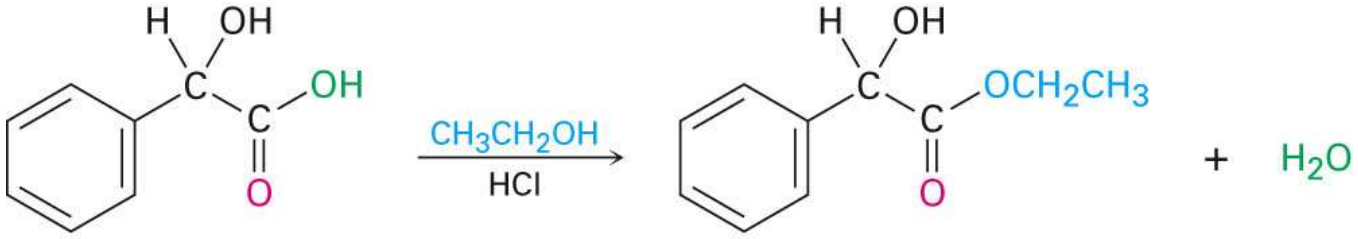
Esterification (Fisher)

Heating a carboxylic acid in an alcohol solvent containing a **small** amount of strong acid produces an ester from the **alcohol** and **acid**



Mandelic acid **Ethyl mandelate (86%)**

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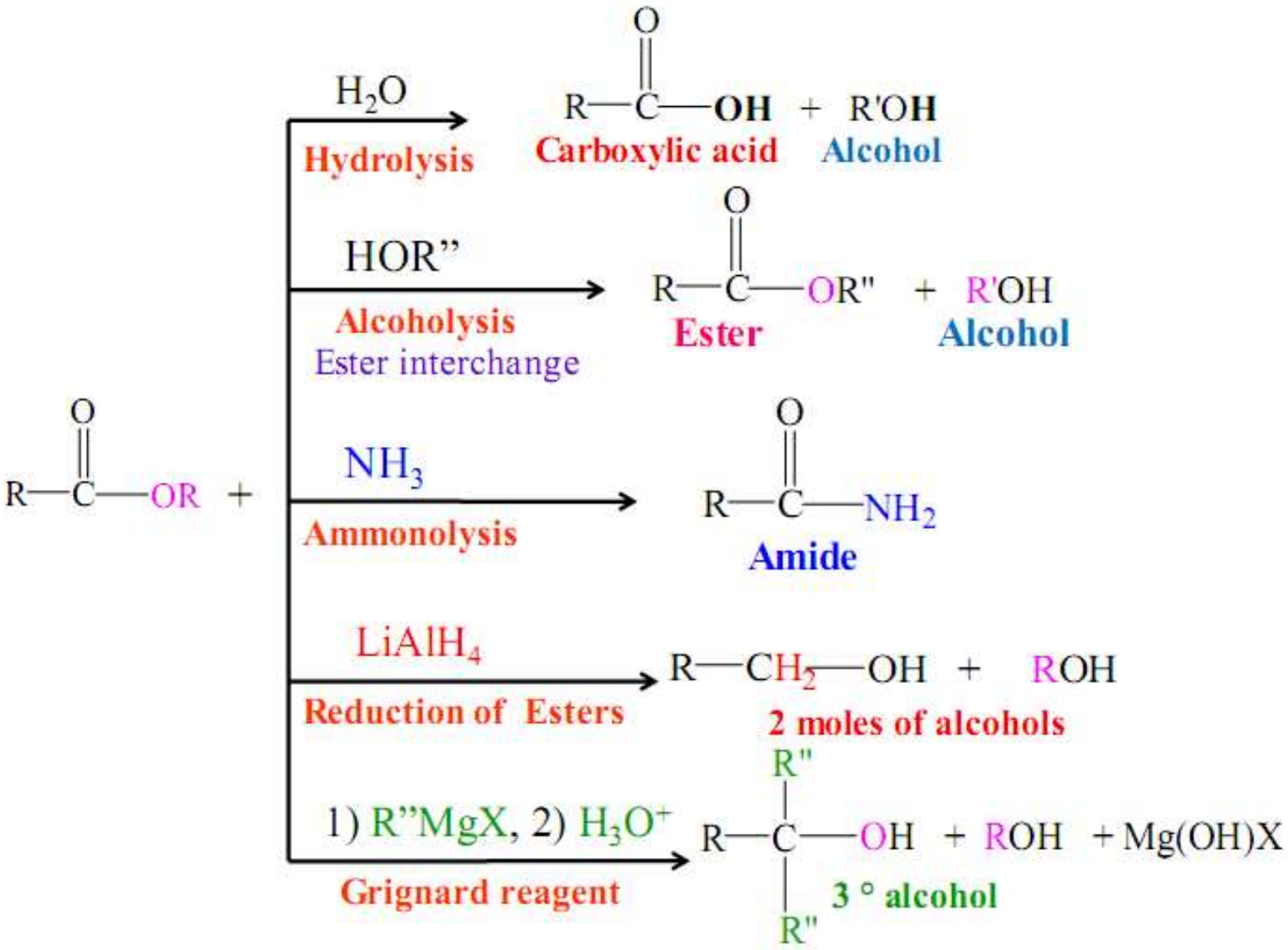
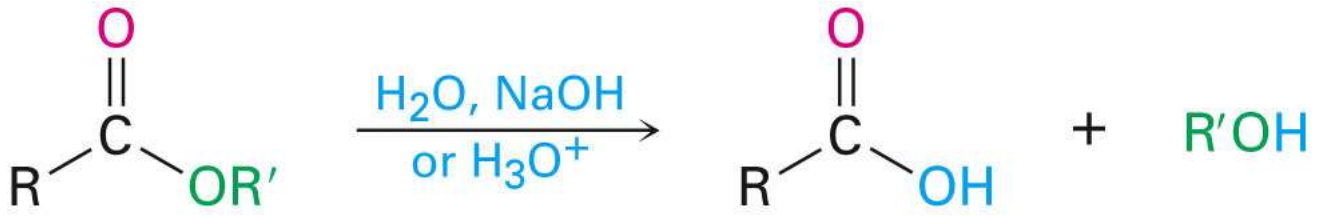
Chemical Properties of Esters



Chemical Properties of Esters

Hydrolysis: Conversion of Esters into Carboxylic Acids

- An ester is **hydrolyzed** by aqueous **base** or aqueous **acid** to yield a carboxylic acid plus an alcohol



Ester **Acid** **Alcohol**

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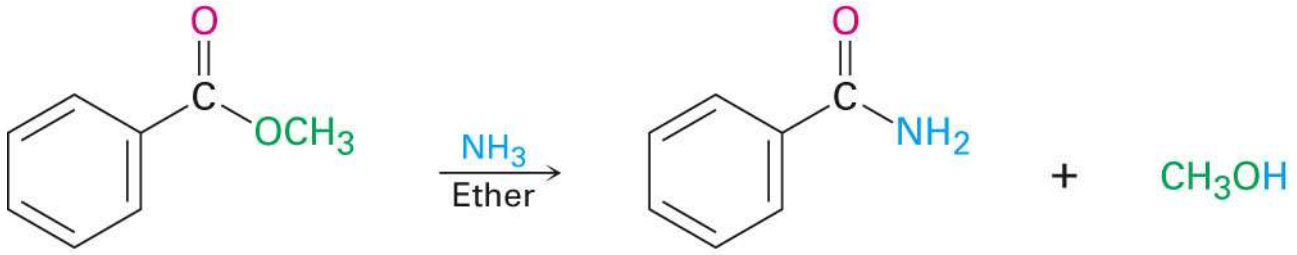
Aminolysis of Esters: Ammonia reacts with esters to form amides



Methyl benzoate **Benzamide**

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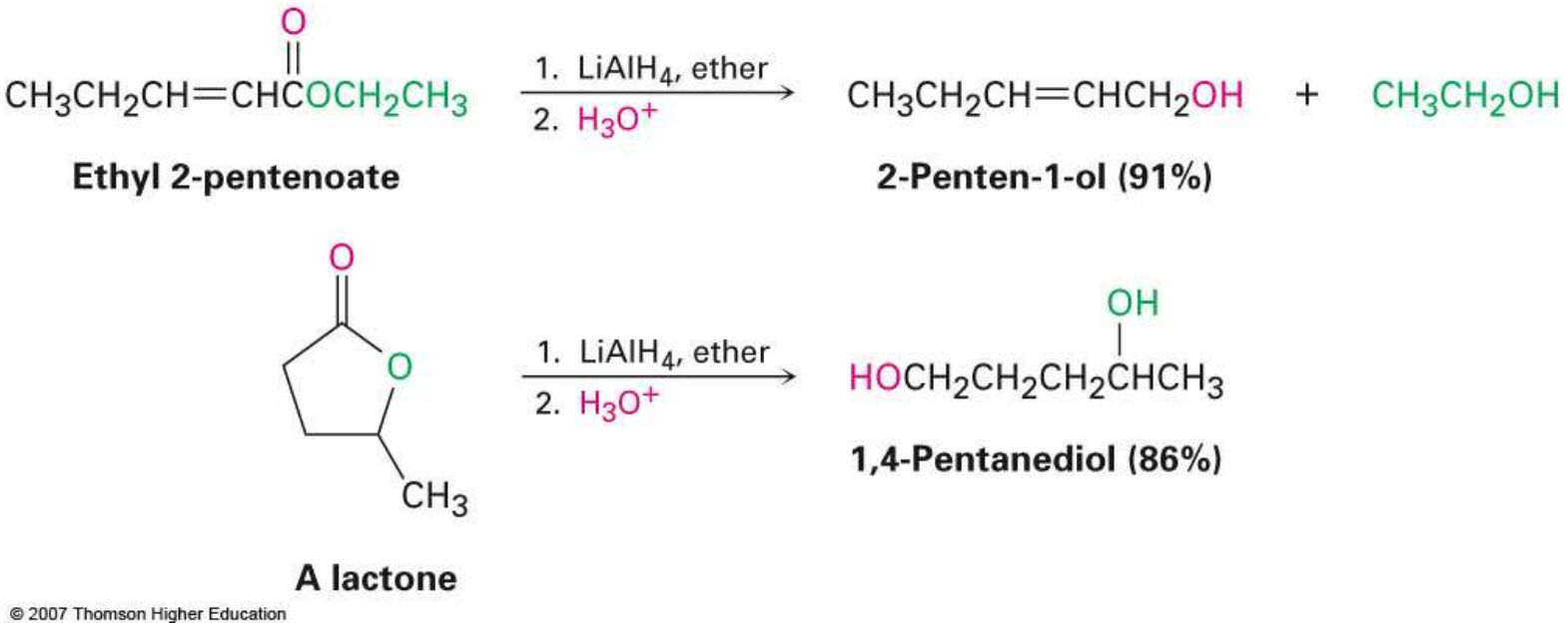
Chemical Properties of Esters

Reduction: Conversion of Esters into **Alcohols** (Reaction with $LiAlH_4$ yields primary alcohols)



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