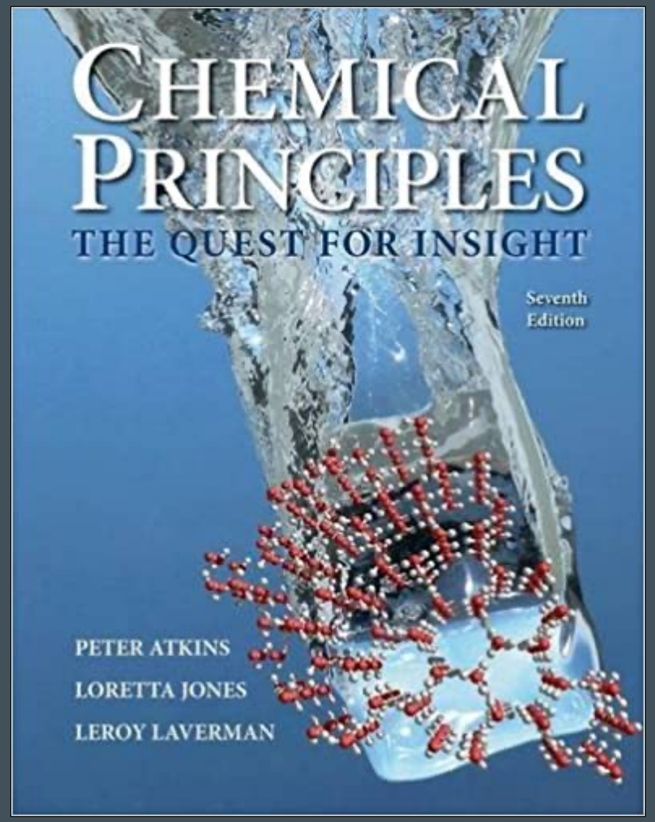
Unit 3 – Deck 2

Organic Chemistry

Functional Groups

Unit 2 Reading

1. *Chemical Principles*
   by Atkins Jones & Laverman
   Chapter 19



Lecture Topics

Section 19.1–19.8

- Haloalkanes
- Alcohols
- Ethers
- Phenols
- Aldehydes & Ketones
- Carboxylic Acids
- Esters
- Amines, Amino Acids, and Amides

Review: Structure of hydrocarbons

Draw the line angle diagrams for the following compounds:

3-ethylhexane

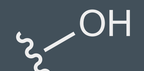
trans-1,2-dimethylethene

6-dimethyl-1,4-octadiene

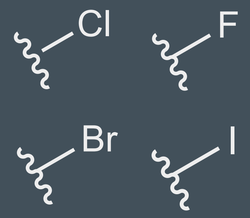
1-butyl-3-propylbenzene

Functional Groups

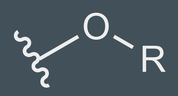
DEF Functional Groups: Characteristic substructures of a molecule that impart unique chemical properties



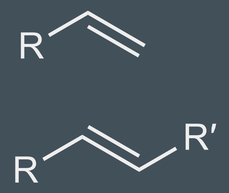
Alcohols



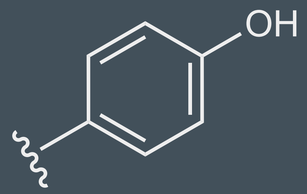
Halides (haloalkanes)



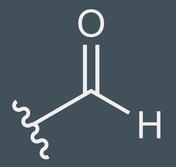
Ethers



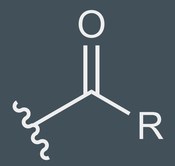
Alkenes (olefins)



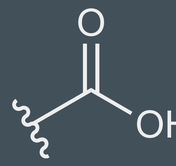
Phenols



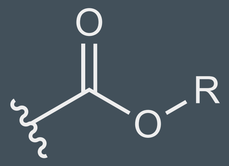
Aldehyde



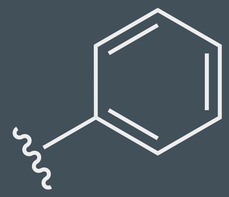
Ketone



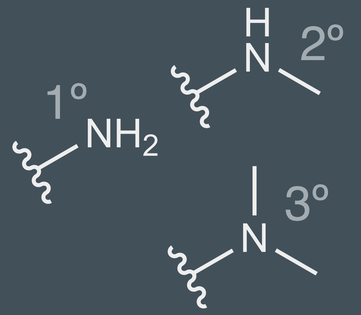
Carboxylic acid



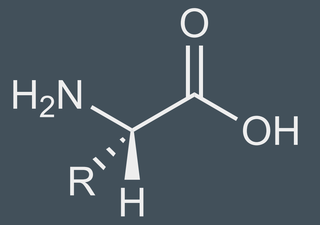
Ester



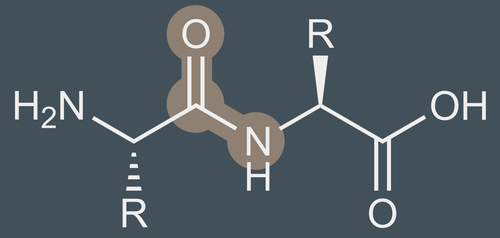
Phenyls



Amines



Amino acid

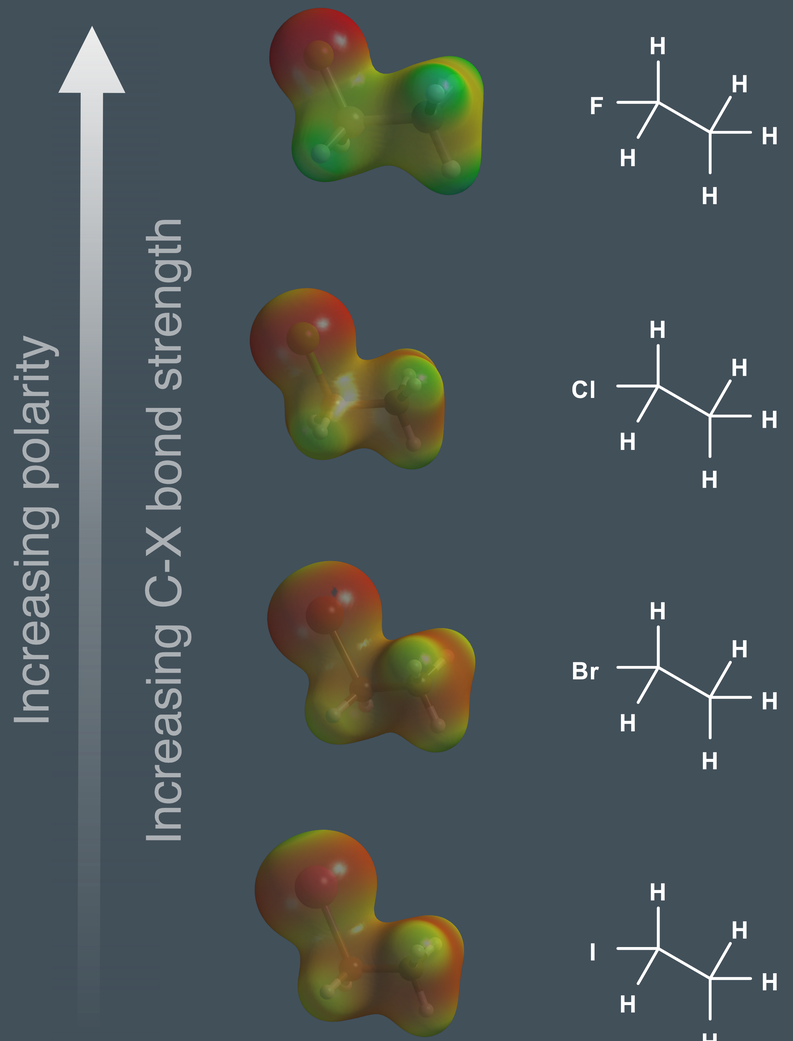


Amide

R = Alkyl

Halides

Electrostatic potential plots



Nomenclature

Fluoro-, Chloro-, Bromo-, Iodo-

or

“methyl fluoride (CH_3F), methylene chloride (CH_2Cl_2), …

2-chloropropane

4-bromobutanol

2-chloro-3-methylbutane

5-iodohexanoic acid

Basic Properties:

- C-F is a very strong polar covalent bond
- C-F alkanes are non-reactive and strongly electron withdrawing (electronegative)
- C-Cl, C-Br, & C-I polarity decreases significantly going down the group.
- C-Cl, C-Br, & C-I are most often used synthetically to create organic compounds with other functional groups.

Haloalkanes – Nucleophilic substitution

The halides Cl, Br, and I are generally good “leaving groups” (weak C–X bonds)

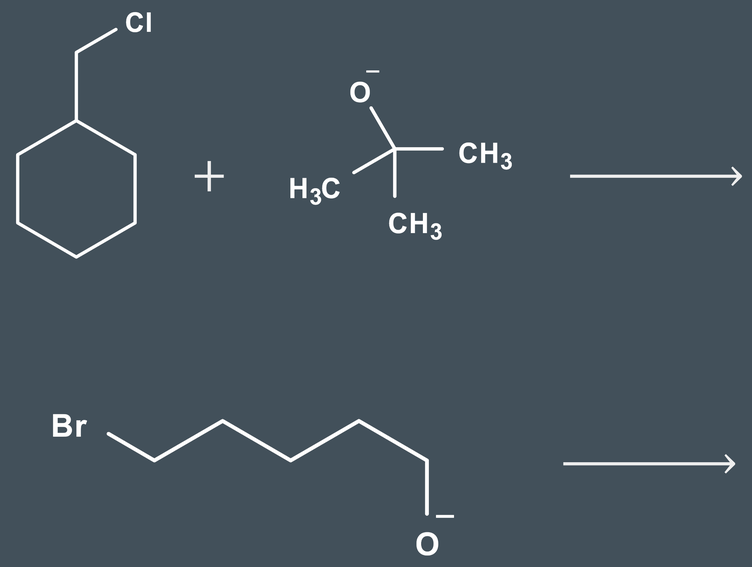
Nucleophilic substitution

C–Br breakage is “heterolytic”: both electrons in the bond go on to form Br^-

Reagents with a high density of electrons on a single atom are generally good nucleophiles

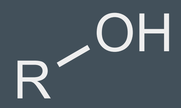
Practice: Nucleophilic substitution

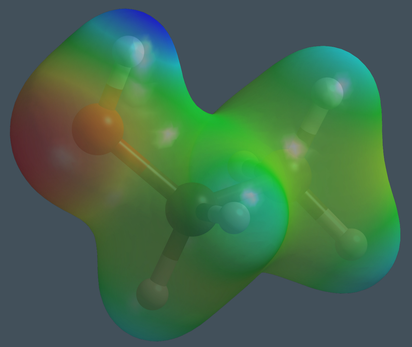
Draw the products of the reaction shown below:



Organic halides are excellent “building block” molecules to form more complex structures

Alcohols and the hydroxyl group





Alcohols are:

- Polar groups
- Hydrogen bond donors
- Hydrogen bond acceptor
- Very weak acids

Nomenclature

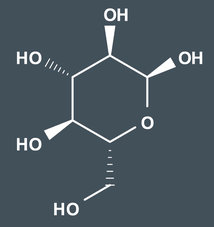
Ethanol or ethyl alcohol

Tert-butanol or tert-butyl alcohol

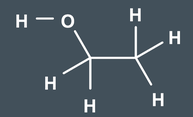
5-hydroxy-hexanoic acid

Synthesis and Properties

Ethanol: Fermentation



$$C_6H_{12}O_6 \xrightarrow{Fermentation} 2\,C_2H_5OH + 2\,CO_2$$



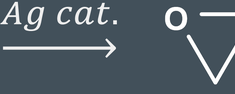
Methanol: Biosynthetically & synthetically accessible.

$$CO\,(g) + H_2(g) \xrightarrow{catalyst,\,250^oC,\,50\,atm} CH_3OH$$

HO — CH_3

Methanol is a starting reagent for acetic acid, formaldehyde, and gasoline additives

Ethylene Glycol: A synthetic *diol*

$H_2C = CH_2 + O_2(g) \xrightarrow{Ag\ cat.}$  $+ H_2O \xrightarrow{Acid\ cat.}$ 

Reagent to form PET

Antifreeze

Glycol	mp = –12 °C
60:40 EG: H_2O	mp = –45 °C
	bp = 110 °C

Practice: Polarity and pKa of alcohols

Acidity of water: $H_2O \rightleftharpoons H^+ + OH^-$ $pKa = 14$

Order these from most to least acidic

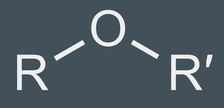
Water

Methanol

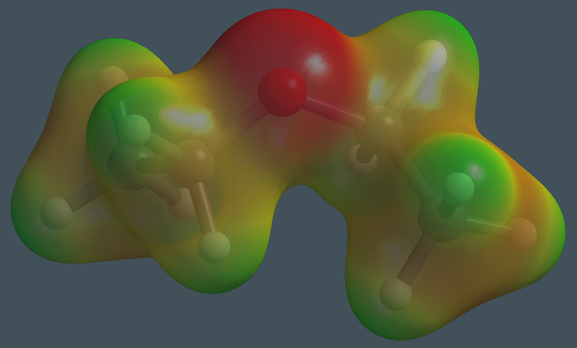
Tert-butanol

2,2,2-Trifluoroethanol

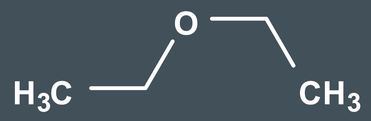
Ethers



An oxygen atom bonded to two different alkyl carbons



diethyl ether



Not very polar
Low boiling points (volatile)

Nomenclature

Methyl ethyl ether

1,2-dimethoxybenzene

Ethyl isopropyl ether

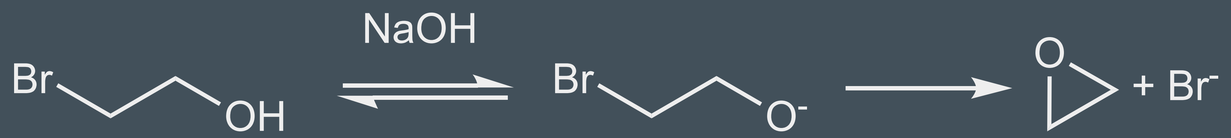
3-chloropropyl ethyl ether

Ethers: Synthesis and Properties

Nucleophilic Substitution:

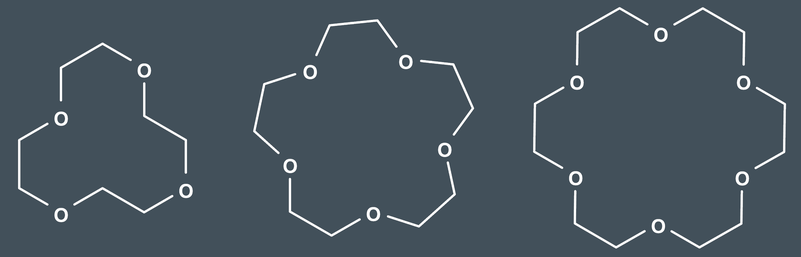
ethyl propyl ether
"1-ethoxy propane"

Nucleophilic Substitution:
Cyclization to form epoxides



an epoxide

Macrocyclic ethers: The Crown Ethers

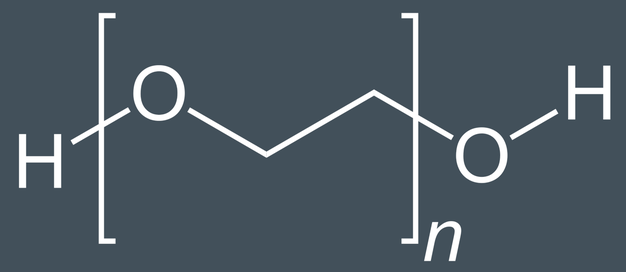


12-crown-4 15-crown-5 18-crown-6

Selective metal binding
18-crown-6

Ethers: Polyethylene glycol

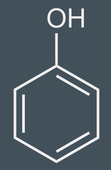
A polyether:

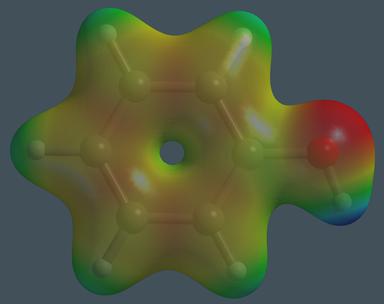


Used everywhere:

- FDA approved biologically inert
  - “PEGylation”: add this group to a drug to make it water soluble
  - Excipient in medications (including the Moderna and Pfizer vaccines)
- Protective coating in art restoration
- Block copolymers (battery electrolytes and elsewhere)
- Component in some rocket propellants
- Toothpaste, skin creams, spandex, body armor, printer ink
- Ceramic binder, emulsifier, CO_2 scrubbing…

Phenols

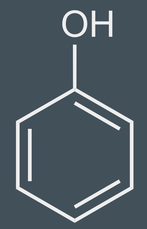




Phenols are weak acids

Phenol: pKa = 10

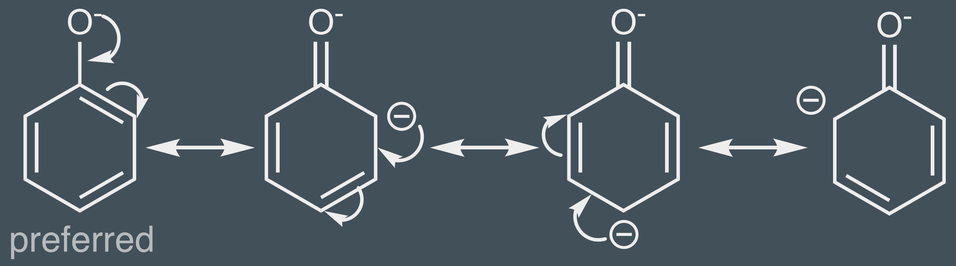
Ethanol: pKa = 15.9



Phenol

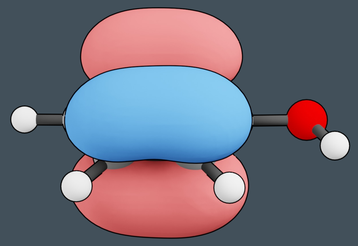
Phenolate

resonance



preferred

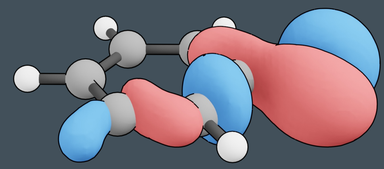
Anion is susceptible to electrophilic addition at carbon



HOMO

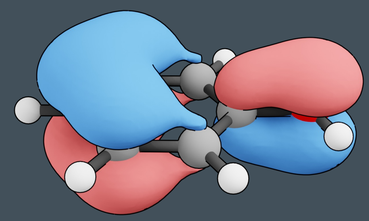
π-donor

Polarized towards ortho



HOMO-1

σ-donor at O



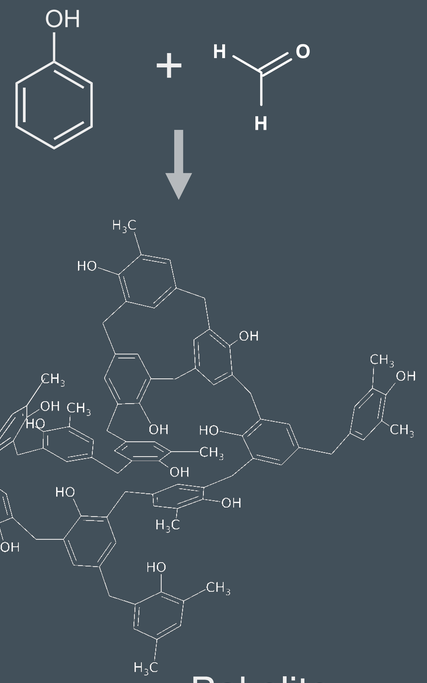
HOMO-2

π-donor

Polarized towards para

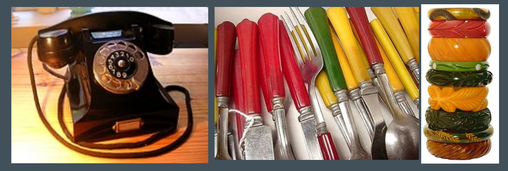
Phenols: useful and biosynthetically diverse

Phenolic Resins



Bakelite

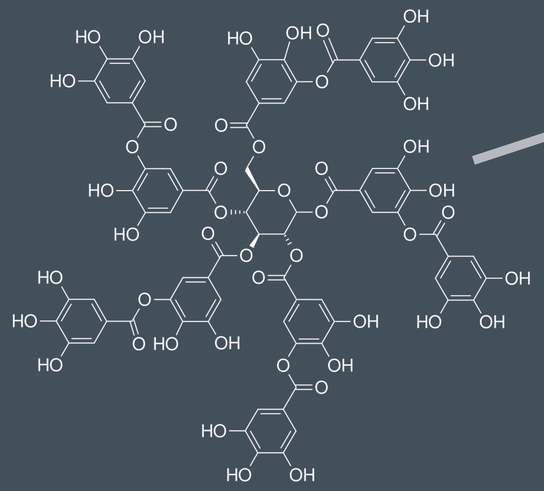
First synthetic polymer
Electronics, jewelry, kitchenware, toys…



Printed circuit boards

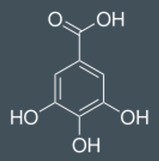
Tannins (polyphenols)

Tannic acid

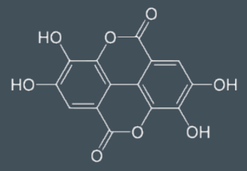


Wine tannins

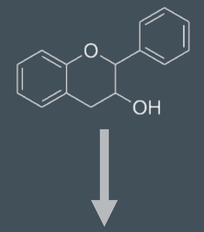
Gallic acid

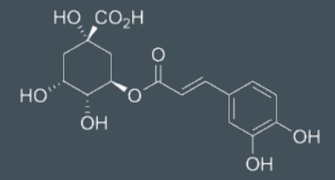


Ellagic acid

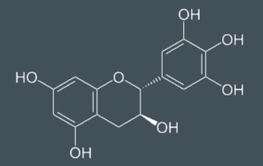


Cacao, tea, acacia, catechu, coffee

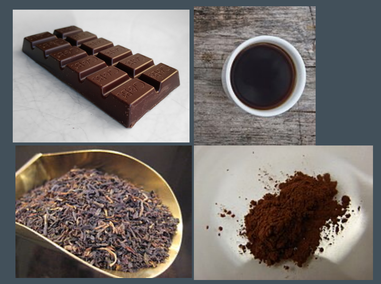




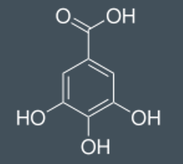
Flavin-3-ols



Chlorogenic acid



Iron Gall Ink

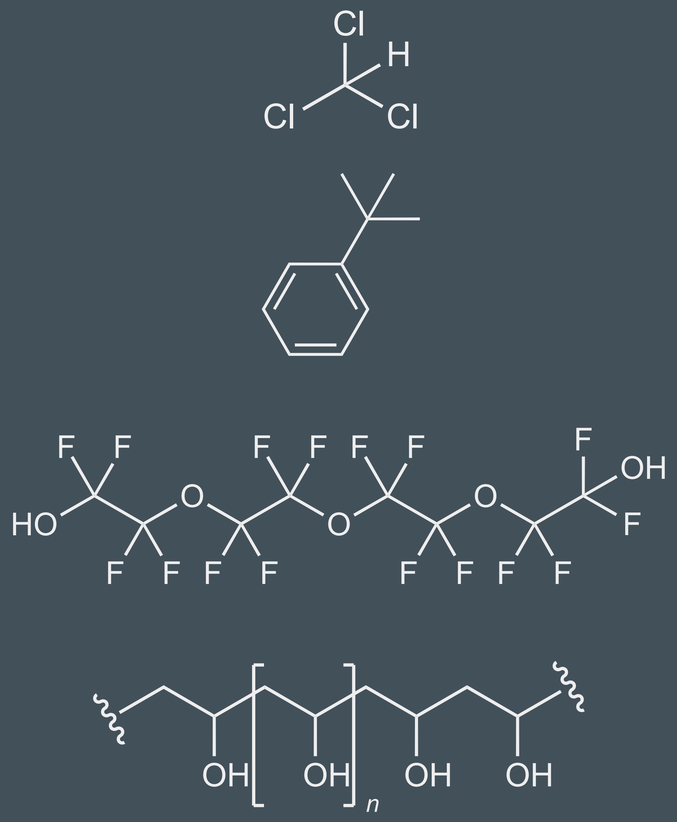


$$Fe(SO_4) \cdot 7H_2O \rightarrow$$

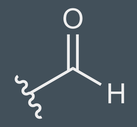
Pliny the Elder *Naturalis Historia*
Drawings of Leonardo da Vinci
USPS official recipe pre-1900

Check-in: Identifying functional groups

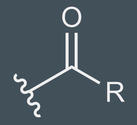
1. What types of functional groups are present?
2. What is the molecular formula?



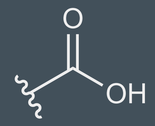
Carbonyl-based functional groups



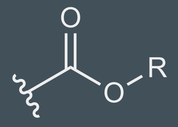
aldehyde



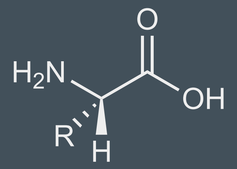
ketone



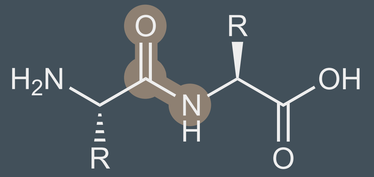
carboxylic acid



ester



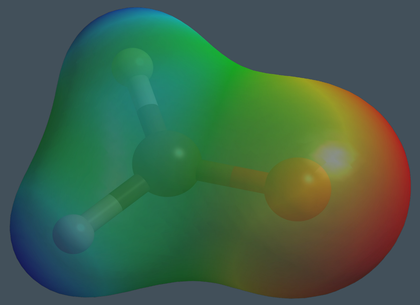
amino acid

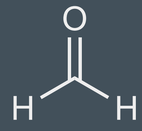


amide

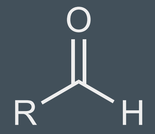
Properties of carbonyl

- Carbonyl: C=O
- Significant dipole
- Diverse chemical reactivity



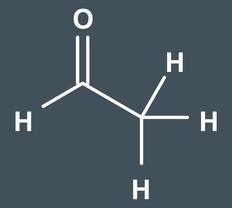
Formaldehyde 

Aldehydes

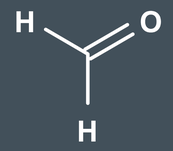


Nomenclature

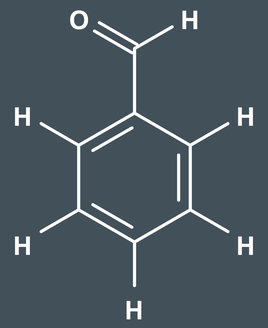
Also called a formyl group



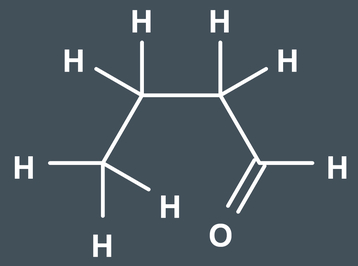
ethanal
acetaldehyde



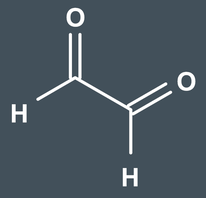
methanal
formaldehyde



phenylmethanal
benzaldehyde



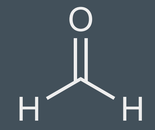
butanal
butyraldehyde



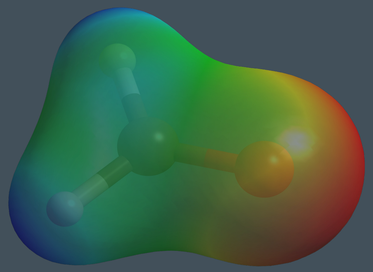
dialdehyde
glyoxal

Synthesis

Oxidation of 1° alcohols

$$2\,CH_3OH + O_2 \rightarrow 2$$  $$+\,2H_2O$$

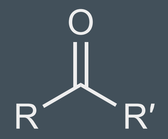
A polar group with an
electrophilic carbon



Applications

- Used as reagents in a vast array of other organic transformations
- Formaldehyde produce at 6 Mt per year (bakelite and other phenolic resins)

Ketones



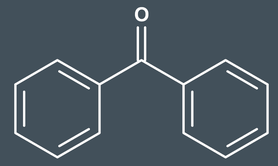
(Like aldehydes but carbonyl is at a 2º carbon)

Nomenclature

Names end with the suffix -one

Acetone = propan-2-one

Parent alkane = propane

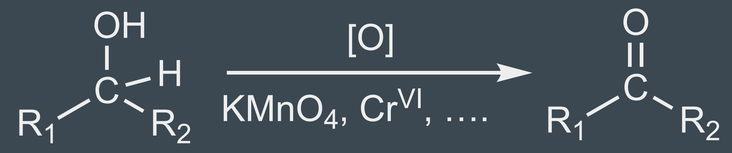


diphenylmethanone

Parent alkane = diphenylmethane

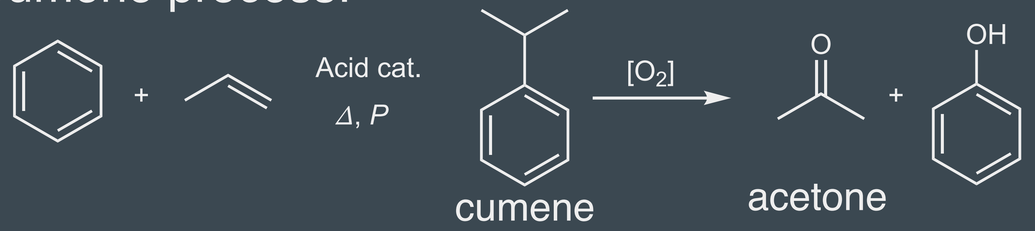
Synthesis of Ketones

Oxidation of 2º alcohols:



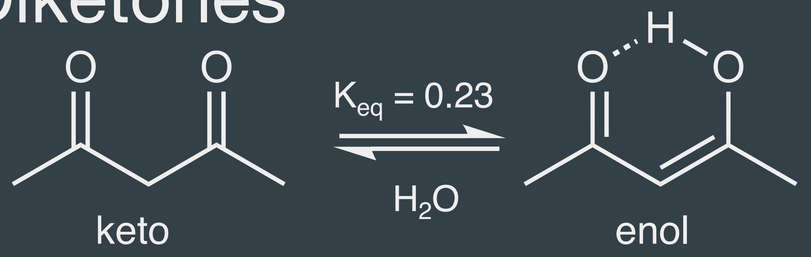
Synthesis of Acetone

Cumene process:



Keto-Enol Tautomerization in 1,3-Diketones

DEF Tautomerization: A dynamic equilibrium between two isomers

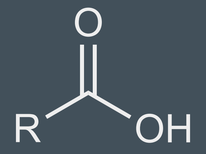


Draw the compound

4-hydroxy-3-methoxybenzaldehyde

2,3-diketobutane

Carboxylic acid



(Like aldehyde but –H is replaced with –OH)

Nomenclature

Suffix –oic acid or –ic acid

Conjugate base: acetic acid --> acetate

Fragrances

Butanoic acid (butyric acid) Rancid butter/barf

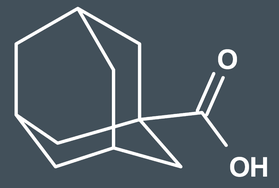
Decanoic acid (capric acid) Goats

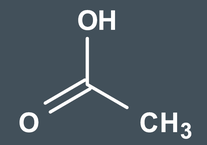
Ethanoic acid (acetic acid) Vinegar

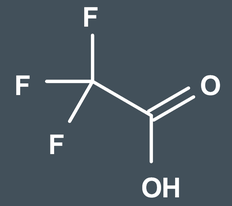
Important fragrance compounds “sour”
(palm oil, chocolate, butter, vanilla, nutmeg, peanut oil…)

Properties

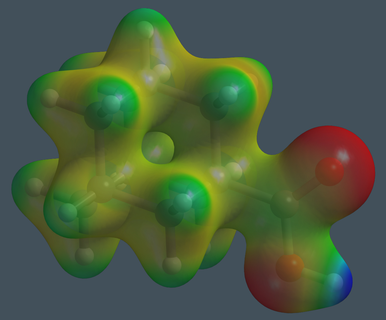
Weak acids pKa ~ 4.5

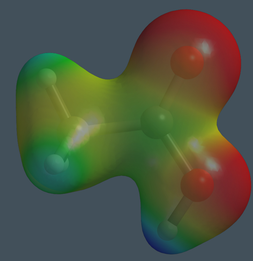


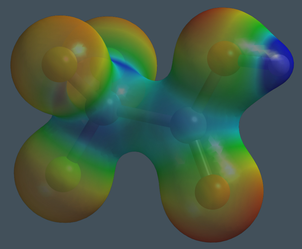




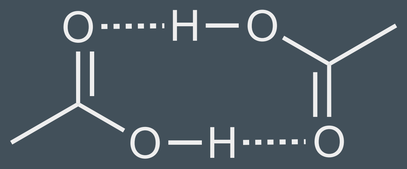
pKa: 4.86* 4.76 0.52







High boiling points:



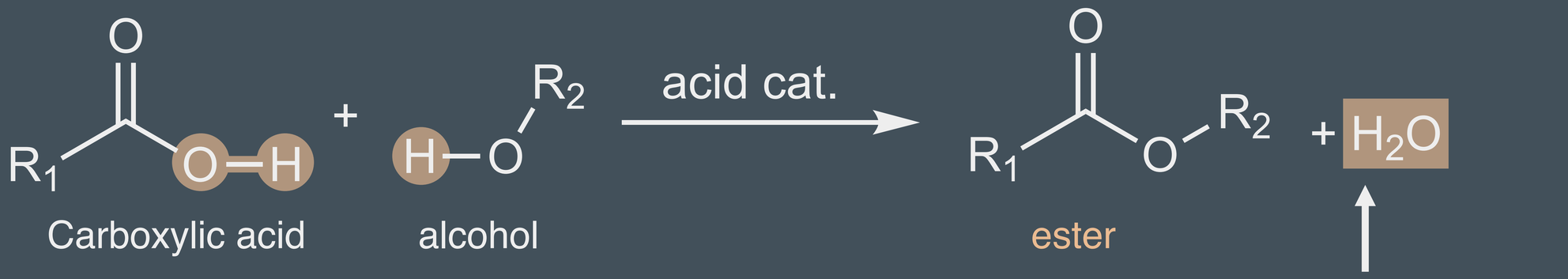
bp = 120 °C

Acid dimers

Condensation reaction of carboxylic acids and alcohols

Two molecules react to form a larger molecule and “expel” as small molecule

Fisher Esterification



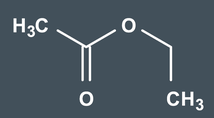
Carboxylic acid alcohol ester

Condensation reactions “condense” water

A simple means of creating more complex molecules from simple building blocks

Esters

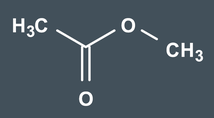
Nomenclature and Flavors (sweet)



Ethyl acetate

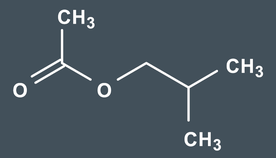
Nail polish remover

Common solvent



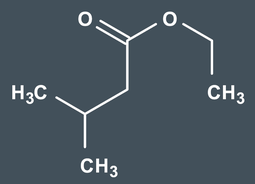
Methyl acetate

Glue



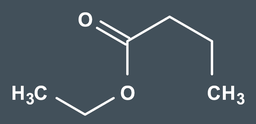
Isobutyl acetate

Cherry, raspberry, strawberry



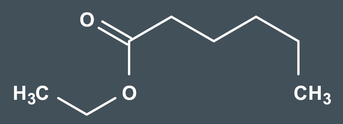
Ethyl 3-methylbutanoate

Apple



Ethyl butyrate

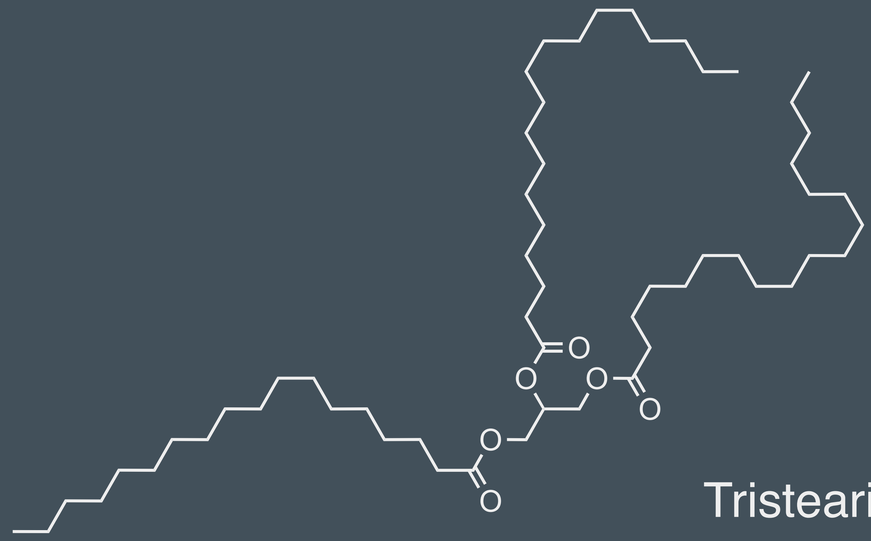
Banana



Ethyl hexanoate

Pineapple

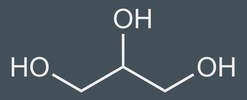
Fats



Tristearin

Fats and oils

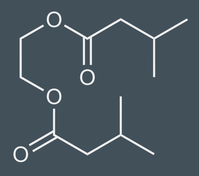
Esters of long chain alkanoic acids & glycerol

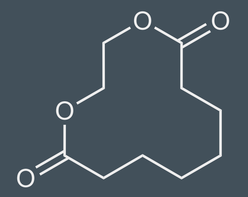


glycerol

Practice: Carboxylic Acids and Esters

What two reactants would you need to form the compound below using a condensation reaction?

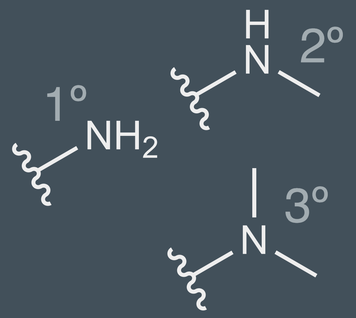




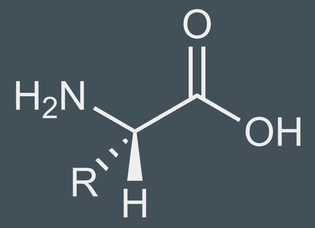
What other products would also be formed during the reaction?

DEF Retrosynthetic Analysis I A strategy in organic synthesis of transforming a target molecule into simpler precursor structures

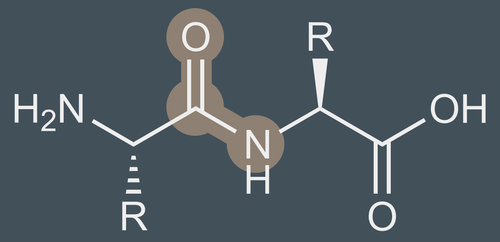
Nitrogen-based functional groups



Amines



Amino acid



Amide

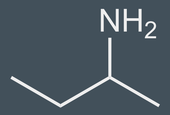
- Nitrogen make three bonds and has one lone pair
- Cationic nitrogen (ammonium) makes four bonds
- The nitrogen lone pair can participate in resonance and act as a Lewis base
- Protic amines N-H are hydrogen bond donors
- The lone pair on Nitrogen is a hydrogen bond acceptor

Amines

Nomenclature (like alcohols)

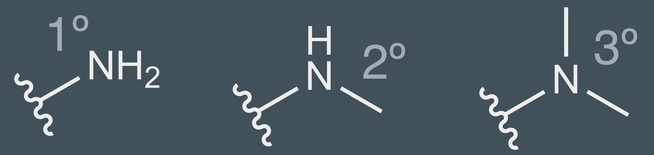
Prefix: amino-
Suffix: -amine

2-amino butane ≡ butan-2-amine

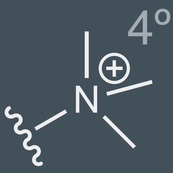


methyl amine H_3C-NH_2

Like carbons, amines can be 1°, 2°, 3° or 4°

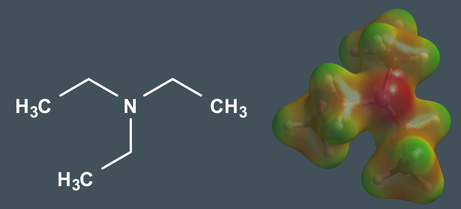


Amines



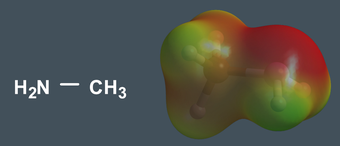
Ammonium

Weak Amine Bases



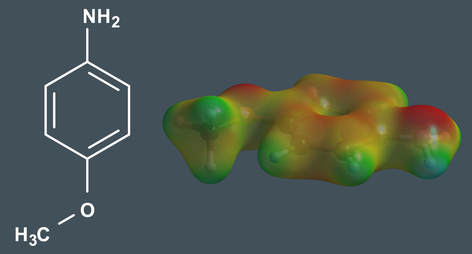
triethylamine

pKa = 10.75



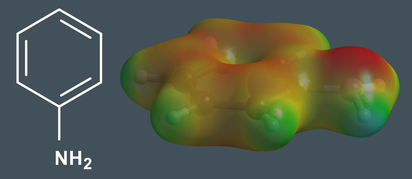
methyl ammonium

pKa = 10.62



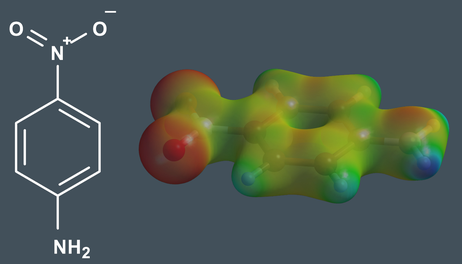
4-methoxyaniline

pKa = 5.36



aniline

pKa = 4.62



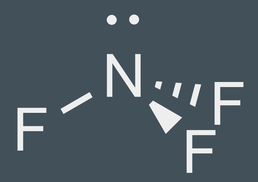
4-nitroaniline

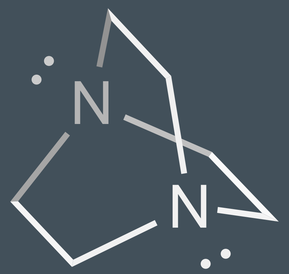
pKa = 1.00

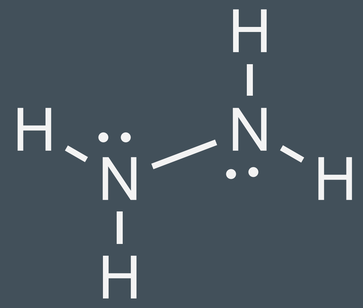
**pKa's of conjugate acids given*

Practice: Basicity of Amines

Order the compounds below from most to least basic:



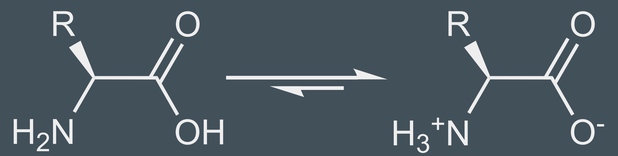




Amino acids

DEF Zwitterion: A charge neutral molecular with other a cationic moiety and an anionic moiety

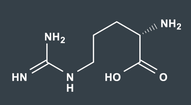
Amino acid



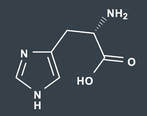
Amino acids are the building blocks of proteins

Ionic side chains

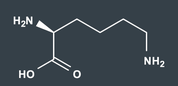
Arginine



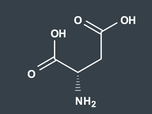
Histidine



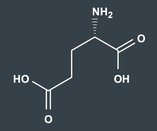
Lysine



Aspartic Acid

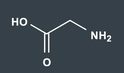


Glutamic Acid

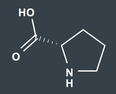


Odd Ducks

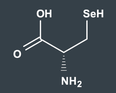
Glycine



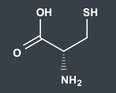
Proline



Selenocysteine

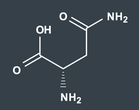


Cysteine

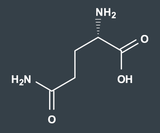


Polar side chains

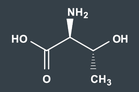
Asparagine



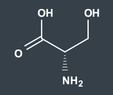
Glutamine



Threonine

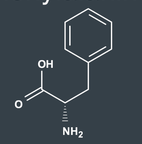


Serine

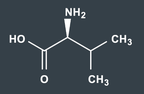


Nonpolar side chains

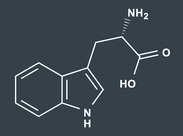
Phenylalanine



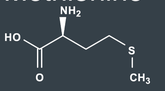
Valine



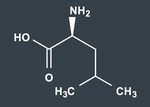
Tryptophan



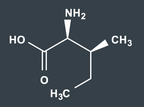
Methionine



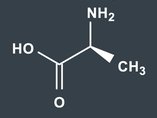
Leucine



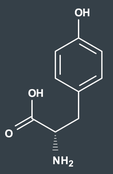
Isoleucine



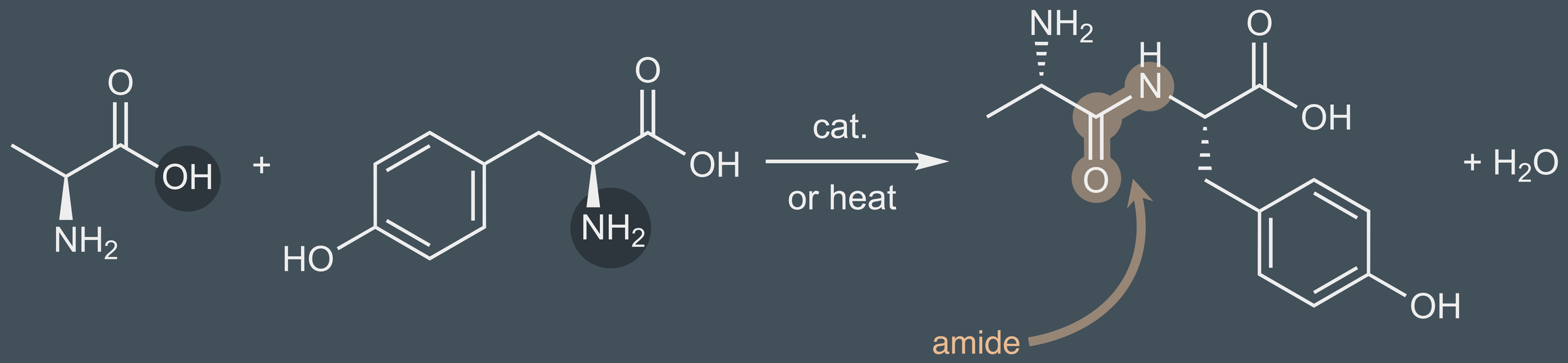
Alanine



Tyrosine



Condensation reactions of amino acids

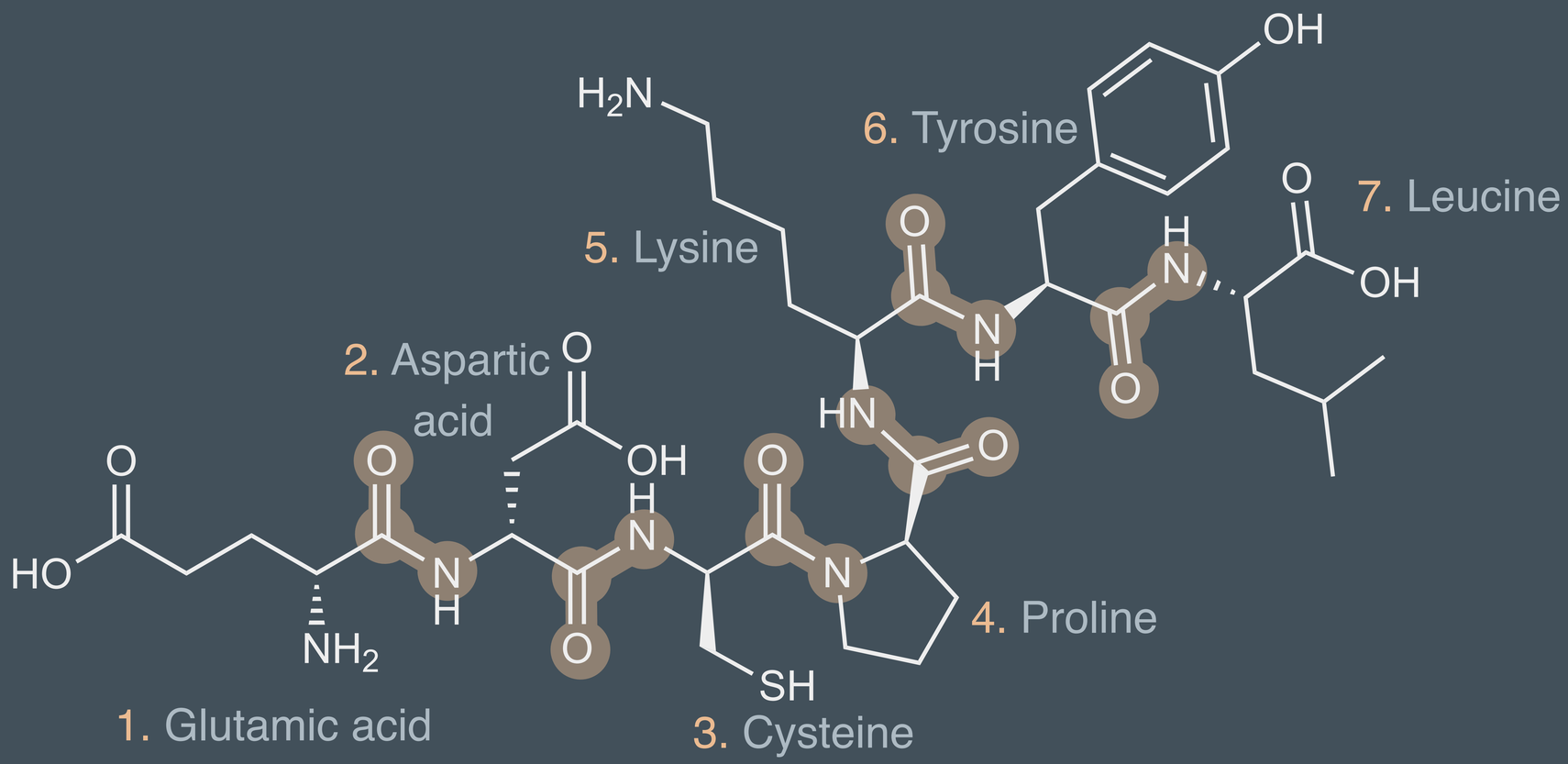


Condensation: Two small molecules react to form one big molecule and one small molecule

Compare to condensation of alcohol and carboxylic acid

Amide Bonds in Peptides

Below seven amino acids form a peptide chain by making amide bonds



Glu-Asp-Cys-Pro-Lys-Tyr-Leu

Larger peptides are called proteins

Practice: Precedence in Naming

1. Carboxylic acids
2. Esters
3. Amides
4. Aldehydes
5. Ketones
6. Alcohols
7. Amines
8. Ethers
9. Alkenes
10. Alkynes
11. Halides
12. Alkanes

If you have more than on functional group there is a convention for naming. The higher on the list the lower the number it gets on the longest carbon chain and or it is preferred as the suffix.