BIO-ORGANIC CHEMISTRY
(Organic Chemistry for Biology Students)
(SQBS 1603)

Organic Compounds Containing Nitrogen

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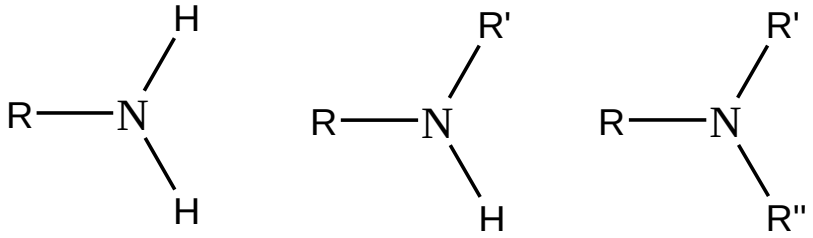
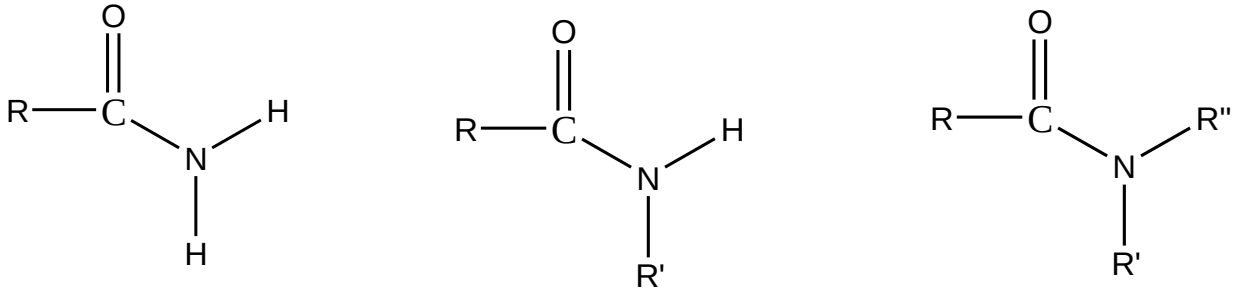
Nitrogen-based functional group

- **Amine: The amino group**
  - **RNH_2**
  - **R_2NH**
  - **R_3N**

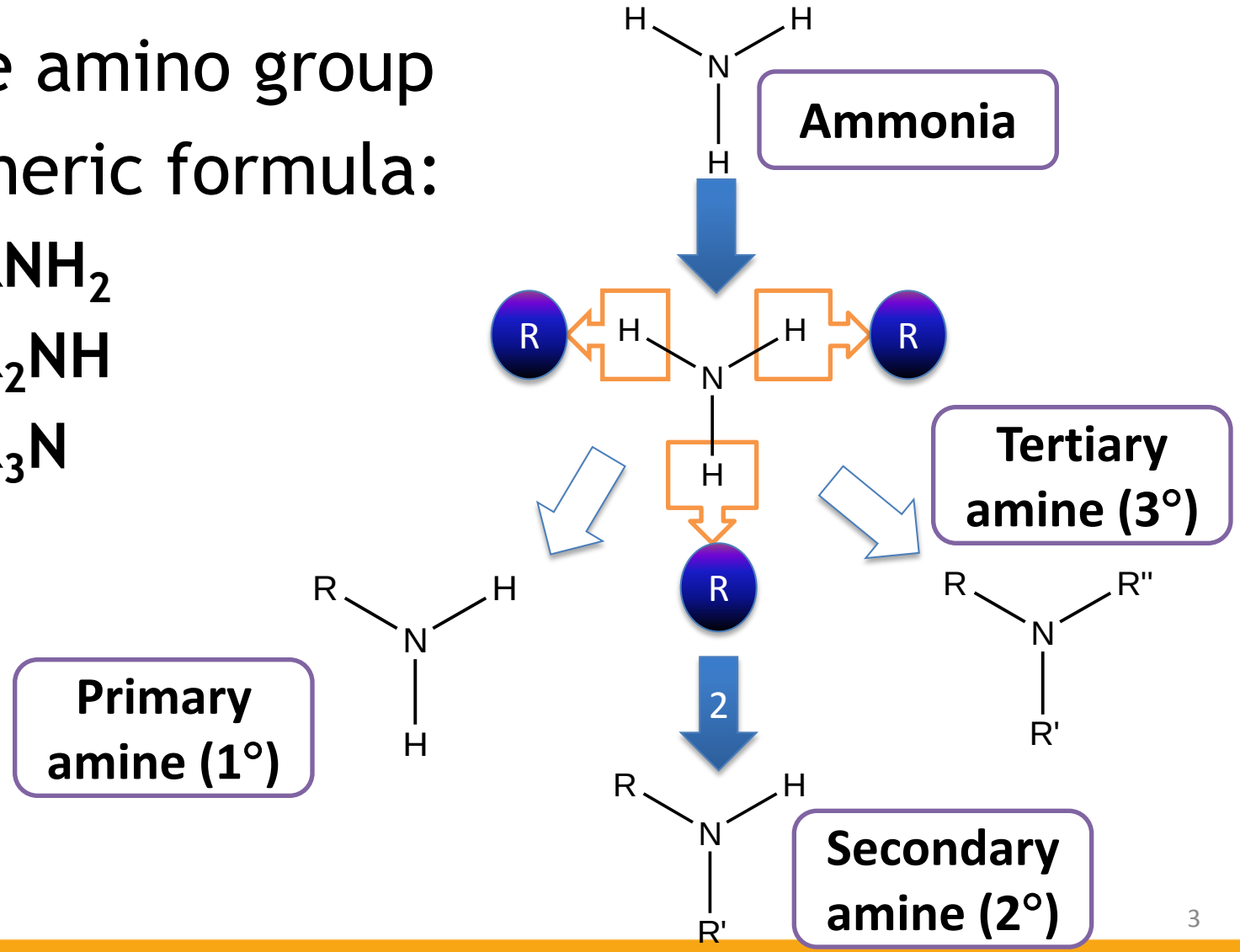


- **Amide: The amide group**
  - **$RCONH_2$**
  - **RCONHR**
  - **$RCONR_2$**



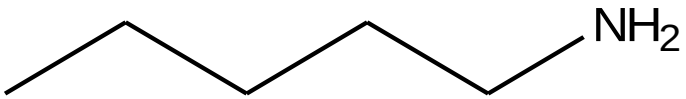
Amines

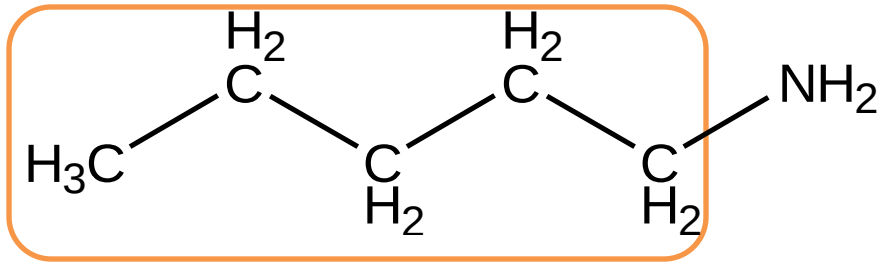
- The amino group
- Generic formula:
  - RNH_2
  - R_2NH
  - R_3N



Naming amines

IUPAC name

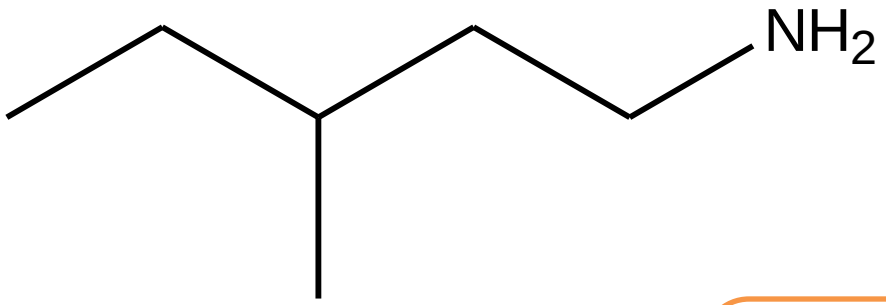




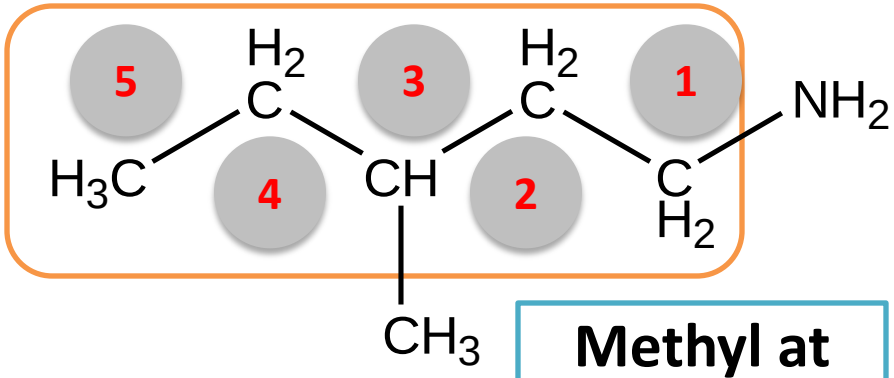
5 C → pentane

Pentanamine

Naming amines



5 C → pentane → pentanamine

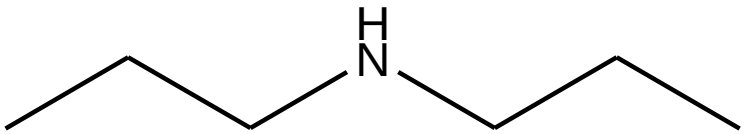


Methyl at position 3

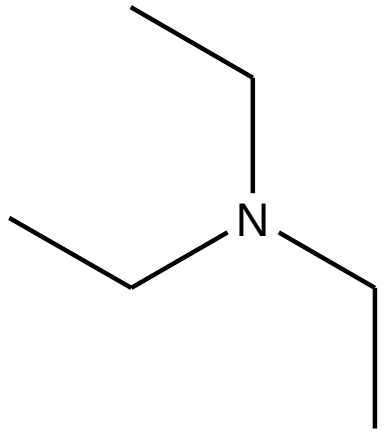
3-methyl-pentanamine

Naming amines

- IUPAC or systematic names of secondary and tertiary amines
  - Secondary (2°) and tertiary (3°) amines having identical alkyl groups are named by using the prefix di- or tri- with the name of the primary amine.
  - Example:



Dipropyl-amine



Triethyl-amine

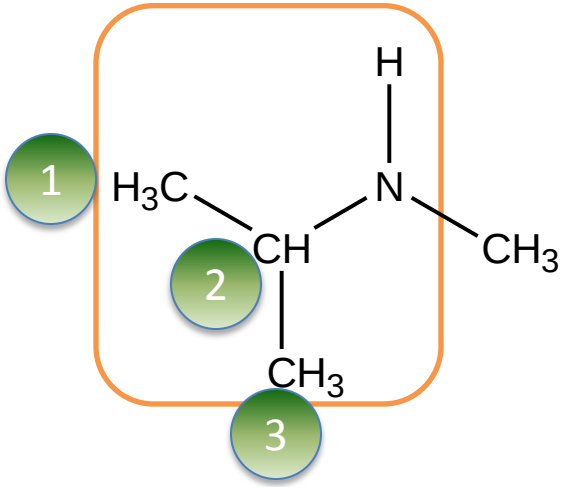
Naming amines

- IUPAC or systematic names of secondary and tertiary amines
  - Secondary (2°) and tertiary (3°) amines having more than one kind of alkyl group are named as ***N-substituted*** primary amines.

Naming amines

Name the following 2° amine: $(CH_3)_2CHNHCH_3$

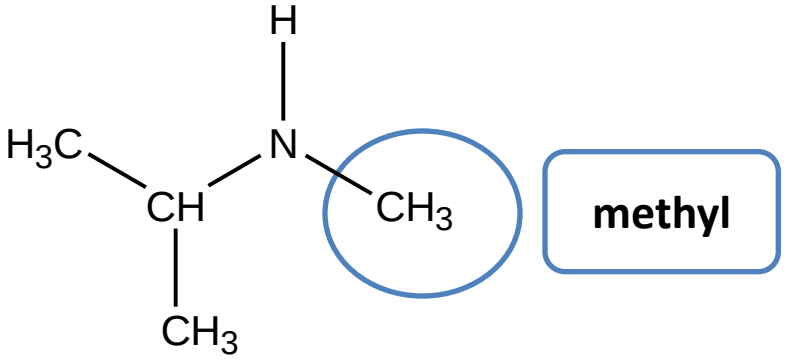
1) Name the longest alkyl chain bonded to the N atom as the parent amine.
   - 3 C → propanamine
   - Since the N atom bonded to the middle C (at position 2) → 2-propanamine



Naming amines

2) Name the other groups on the N atom as alkyl group

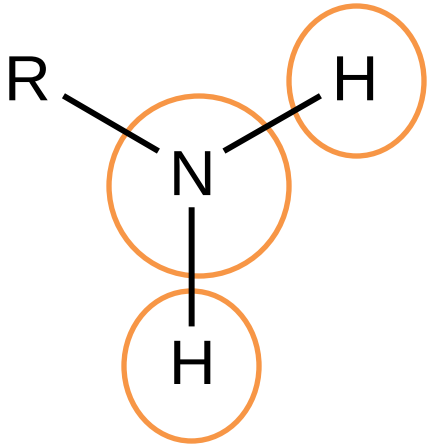
- alphabetize the names when there is more than one substituent
- Precede each name with the prefix *N*-.



N-methyl-2-propanamine

Physical properties of amines

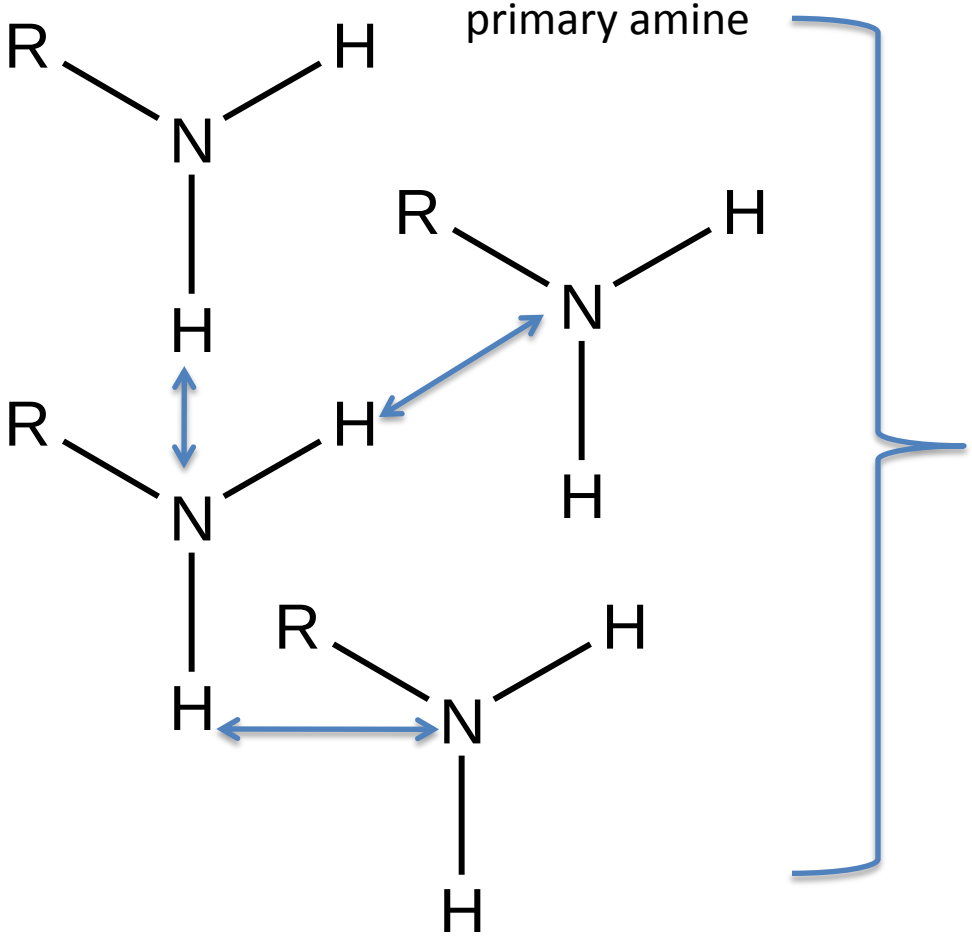
- Physical property of primary amine



N (nitrogen) → electronegative atom → polar molecule

Hydrogen bonding?

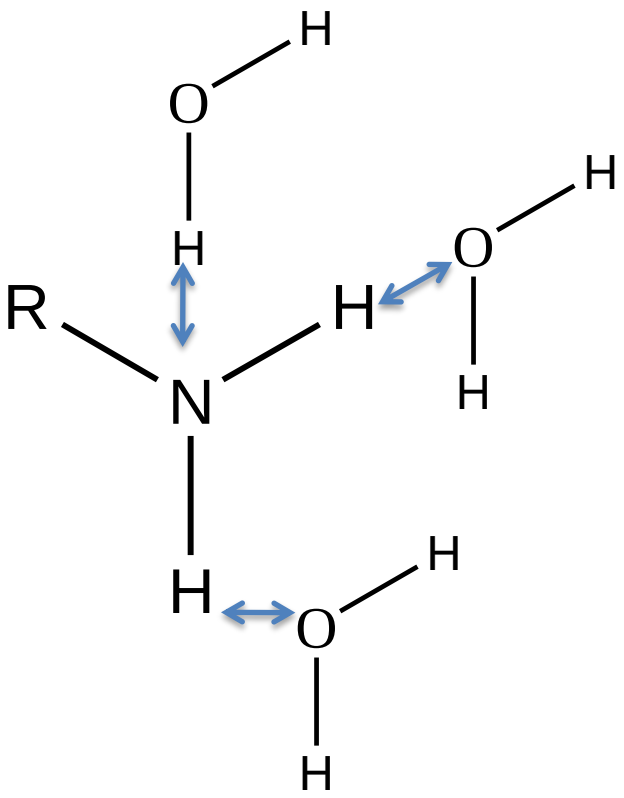
Physical properties of amines



- **Hydrogen bonding between molecules of same compound.**
- **Up to 3 hydrogen bonds can occur for primary amine.**

Physical properties of amines

primary amine

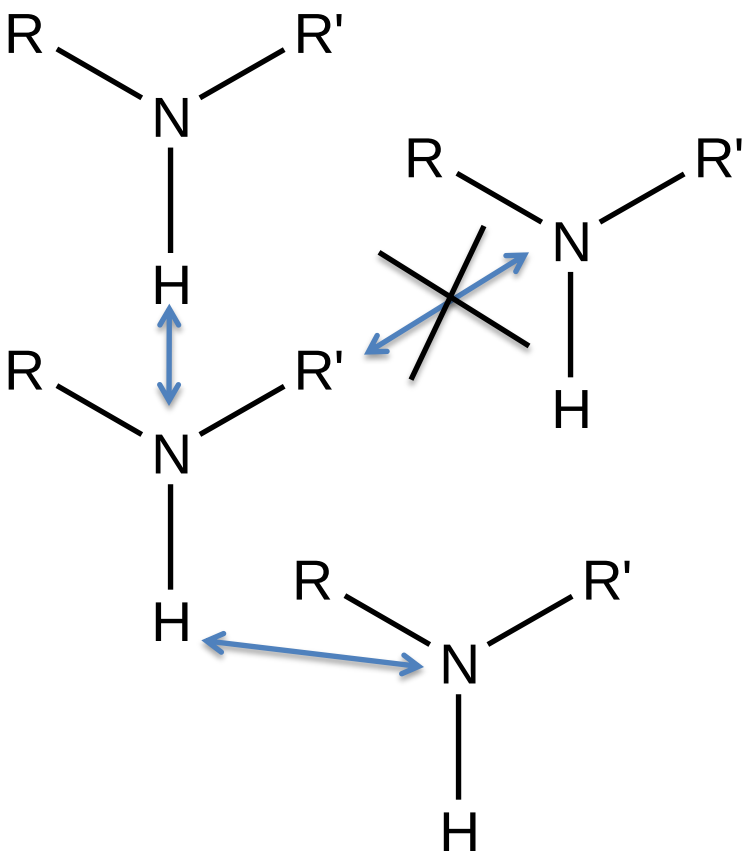


❖**Hydrogen bonding with water.**

❖**Up to 3 hydrogen bonds can occur for primary amine.**

Physical properties of amines

secondary amine

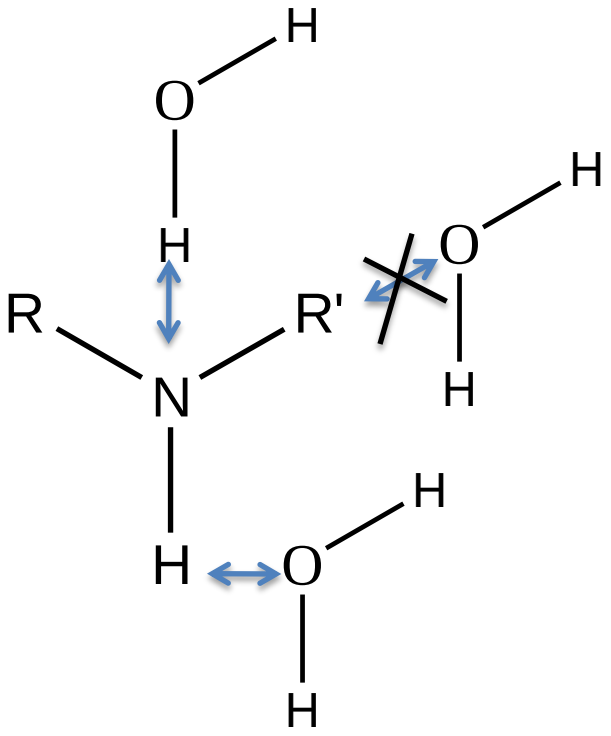


❖**Hydrogen bonding between molecules of same compound.**

❖**Up to 2 hydrogen bonds can occur for secondary amine.**

Physical properties of amines

secondary amine

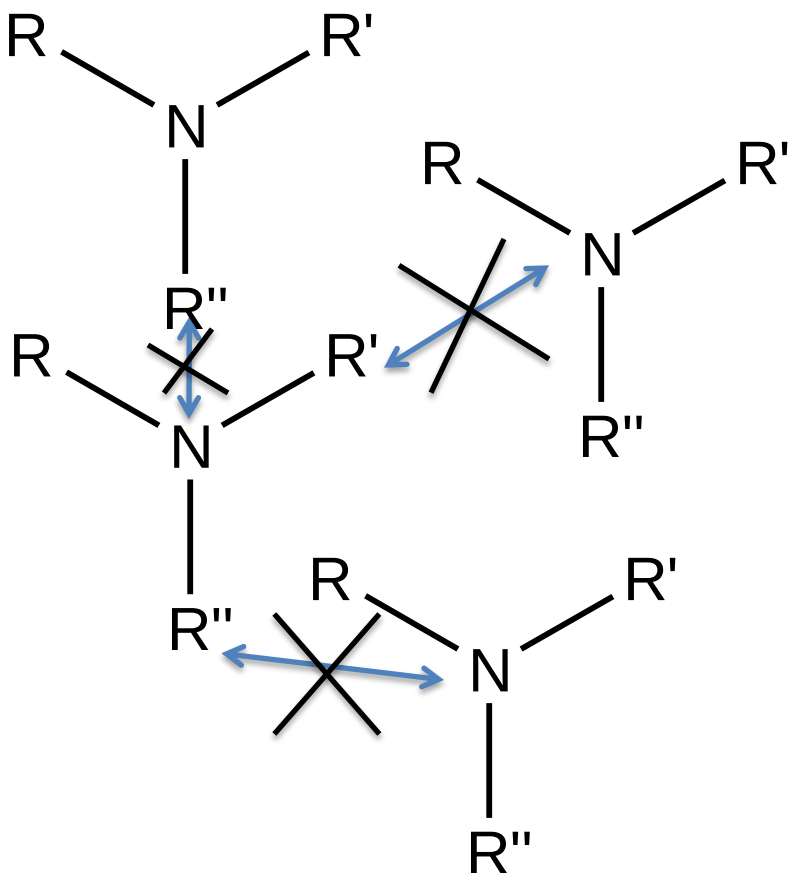


❖**Hydrogen bonding with water.**

❖**Up to 2 hydrogen bonds can occur for secondary amine.**

Physical properties of amines

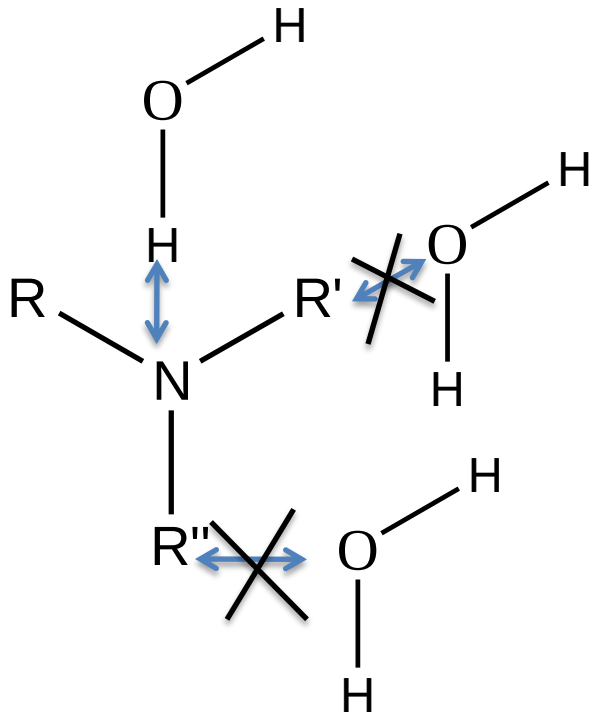
Tertiary amine



❖**No hydrogen bonding between molecules of same compound for tertiary amine.**

Physical properties of amines

Tertiary amine

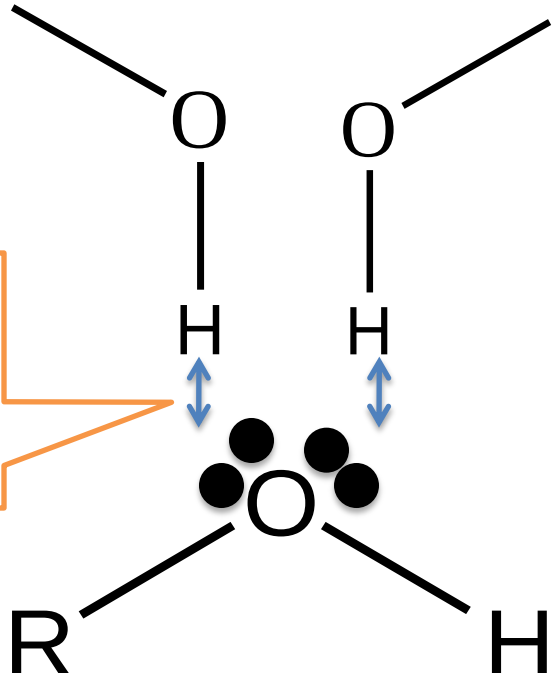


❖**Hydrogen bonding with water.**

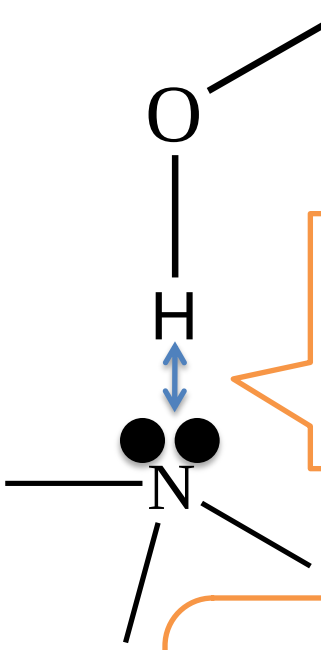
❖**Only 1 hydrogen bonds can occur for tertiary amine.**

Physical properties of amines

- Comparison with other organic compounds
  - alcohol



Two lone pair can participate in 2 hydrogen bonds



One lone pair participates in only one hydrogen bond

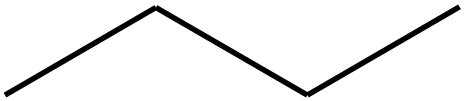
Results:
- **amines have lower melting and boiling points than alcohol.**

Physical properties of amines

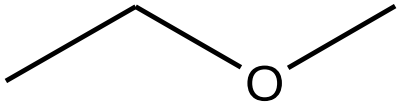
- The general rule
  - For compounds of comparable size
    - The stronger the intermolecular forces (forces between molecules of same compounds) → the higher the boiling points.
  - Compounds that can hydrogen bond have higher boiling points than compounds that are polar but cannot hydrogen bond.
  - Polar compounds have higher boiling points than nonpolar compounds.

Physical properties of amines

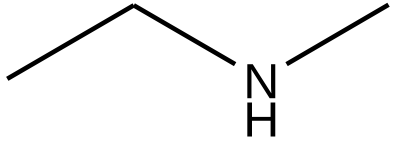
- Which compound has the higher boiling point?



Butane



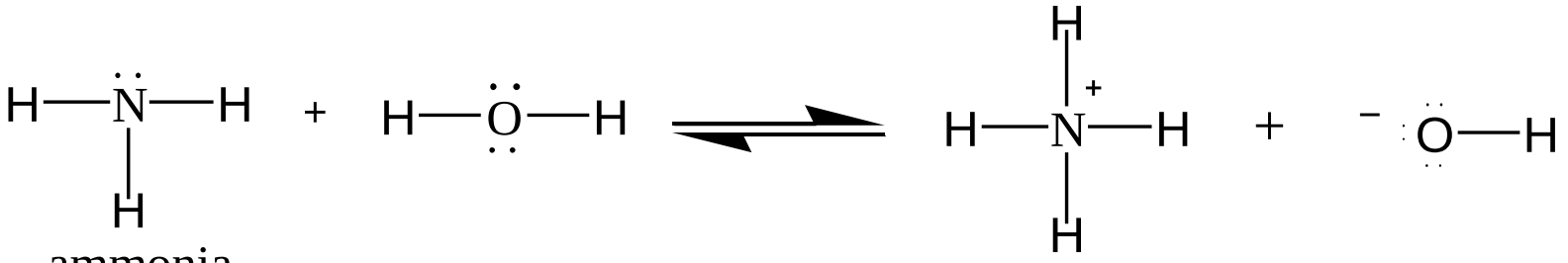
Methoxy-ethane



Ethyl-methyl-amine

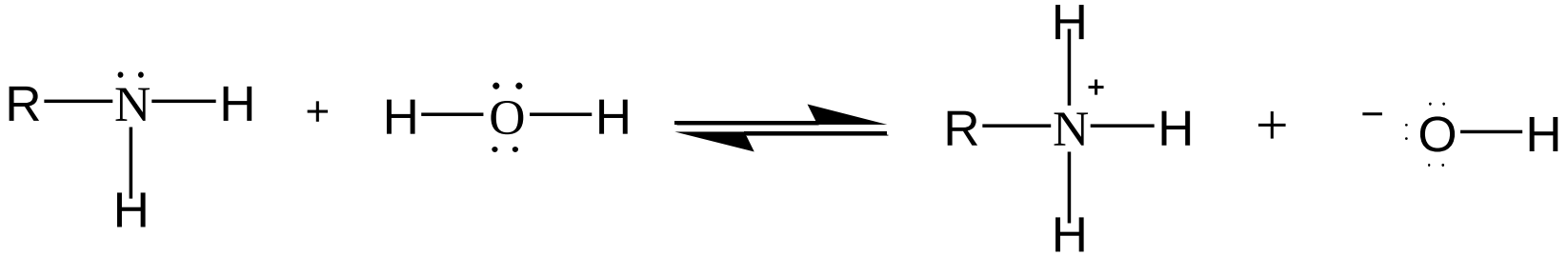
Amines as bases

- Amines are proton acceptor



ammonia

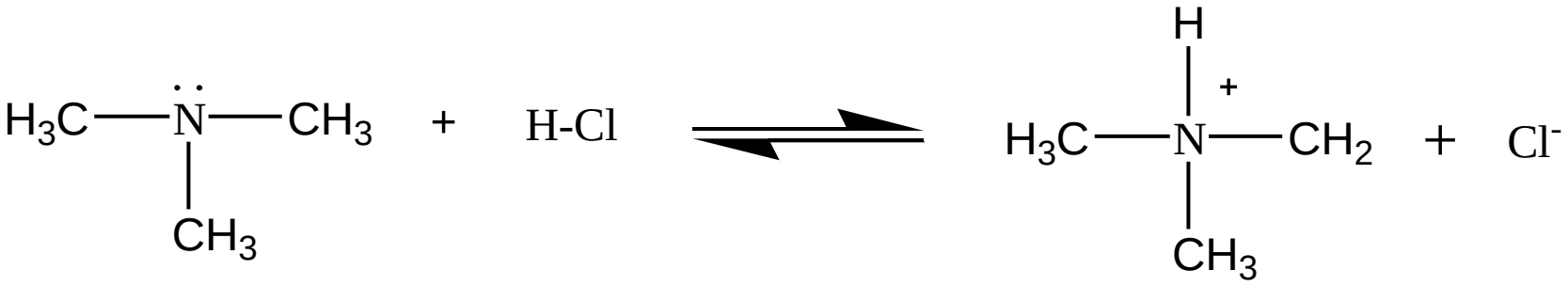
ammonium ion



primary amine

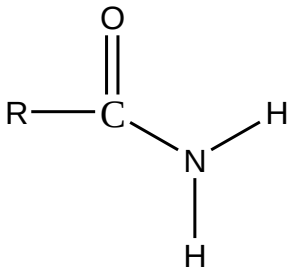
Reaction of amines with acids

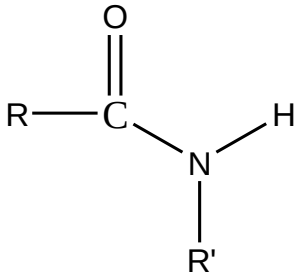
- Amines react with acids such as HCl to form water-soluble salts
- Amine gains a proton to form its conjugate acid (ammonium cation)
- A proton is removed from the acid to form its conjugate base
- Example:

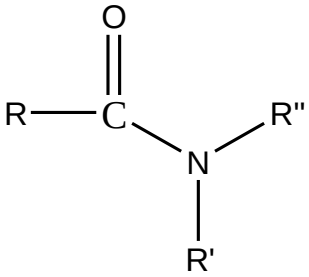


Amides

- The amide group
- Generic formula:
  - $RCONH_2$
  - RCONHR
  - $RCONR_2$

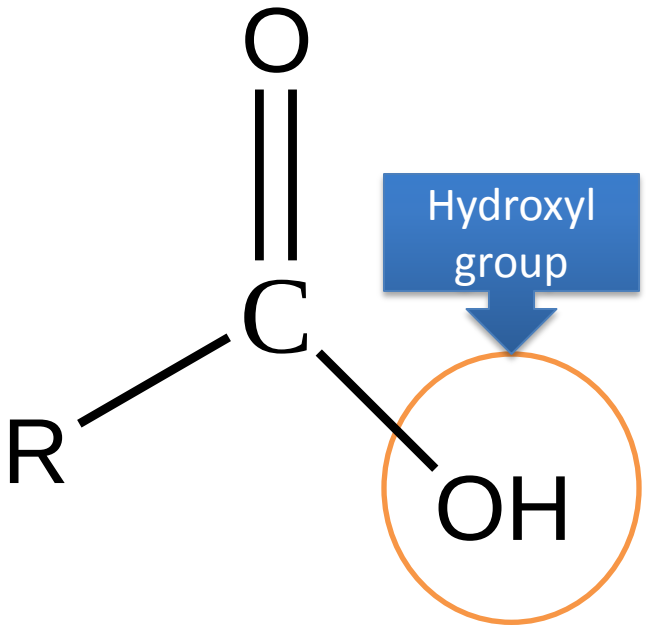




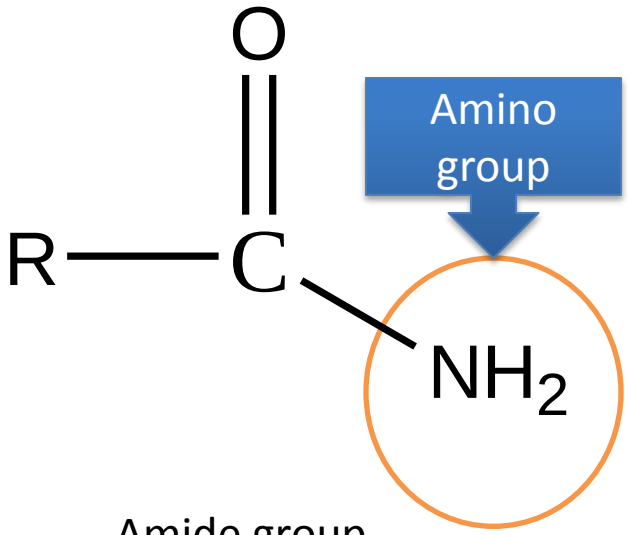


Amides

- Amide group closely resembles the carboxyl group of carboxylic acid



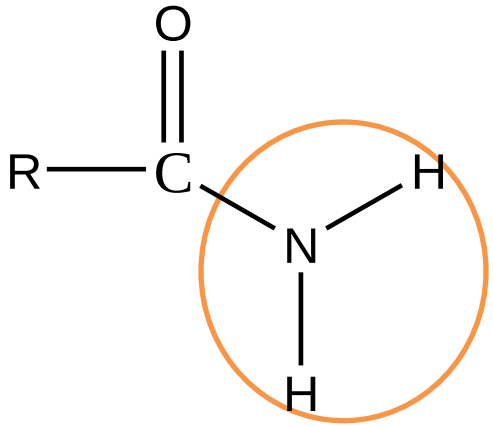
carboxyl group of carboxylic acid



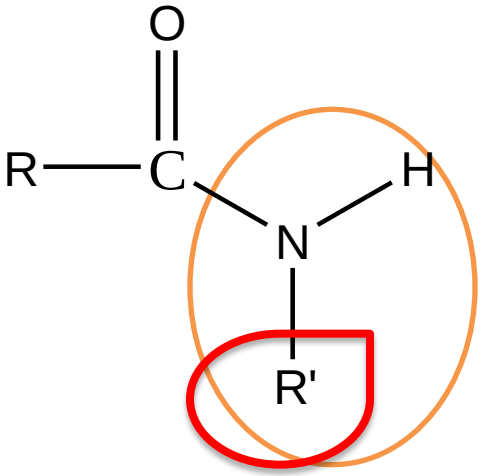
Amide group

Amides

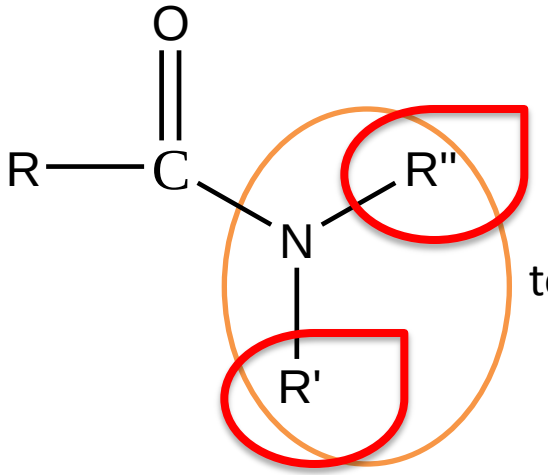
- Primary, secondary and tertiary amide



Primary



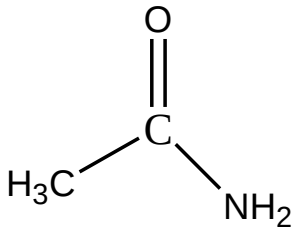
secondary

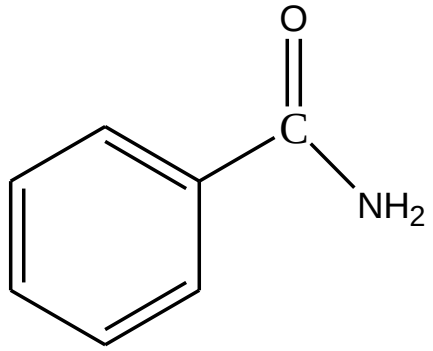


tertiary

Naming amides

- In the IUPAC system, amides are identified by the suffix *-amide*.
- If primary amide
  - Replacing -oic acid ending (or -ic acid ending of a common name) with the suffix -amide
  - Examples





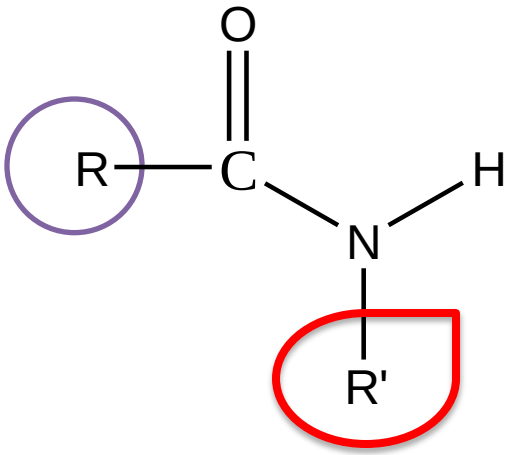
Derived from ethanoic acid (acetic acid) → **Ethanamide (acetamide)**

Derived from benzoic acid → **benzamide**

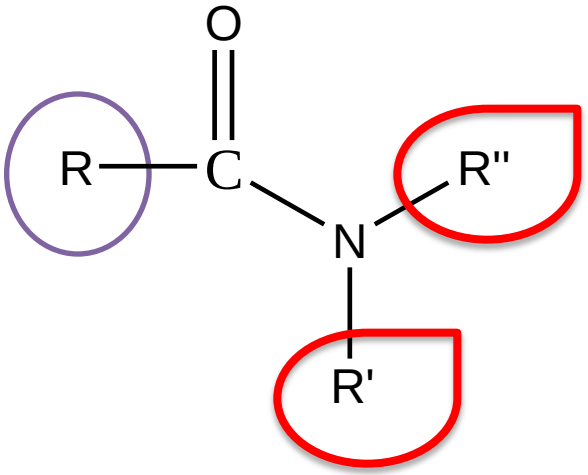
Naming amides

- Secondary (2°) and tertiary (3°) amides.
  - Acyl group: attach to carbonyl group.
  - Alkyl group: attach to N.

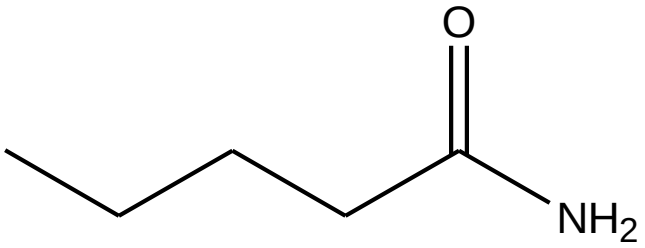
secondary



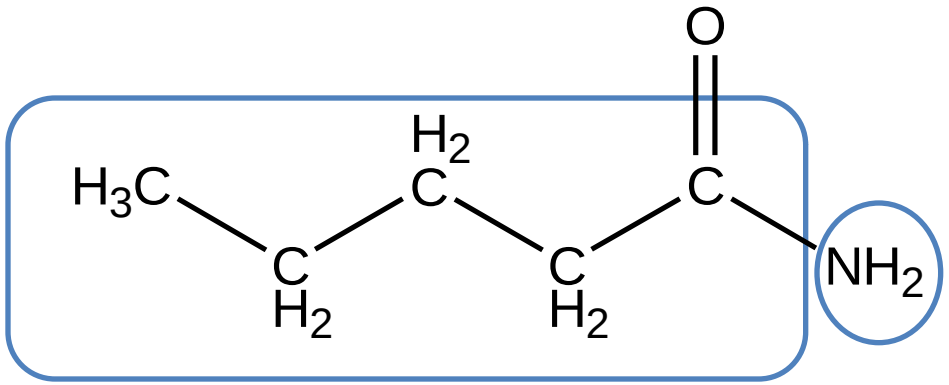
tertiary



Naming amides



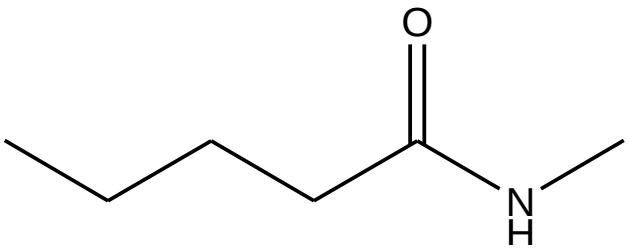
5 C → pentane → pentanamide



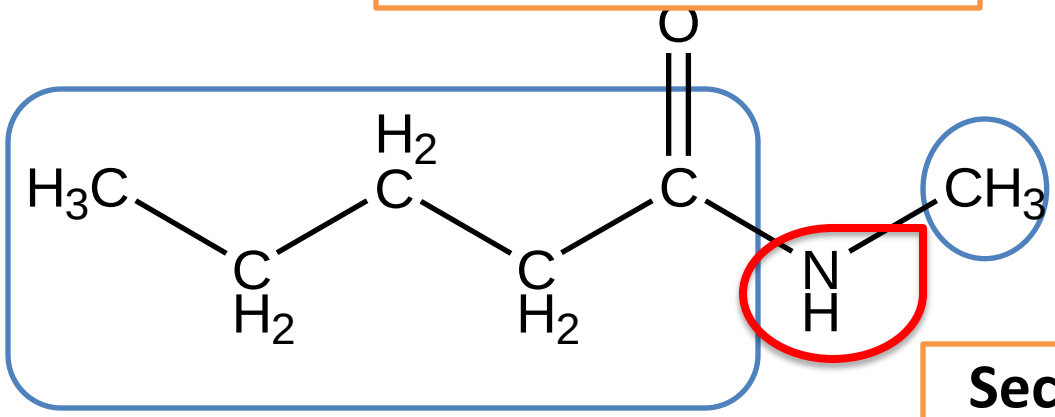
Primary (1°) amine

pentanamide

Naming amides



5 C → pentane → pentanamide

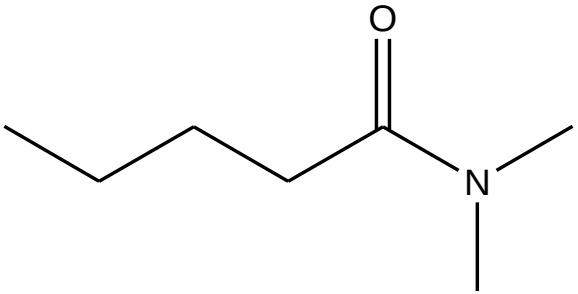


Methyl

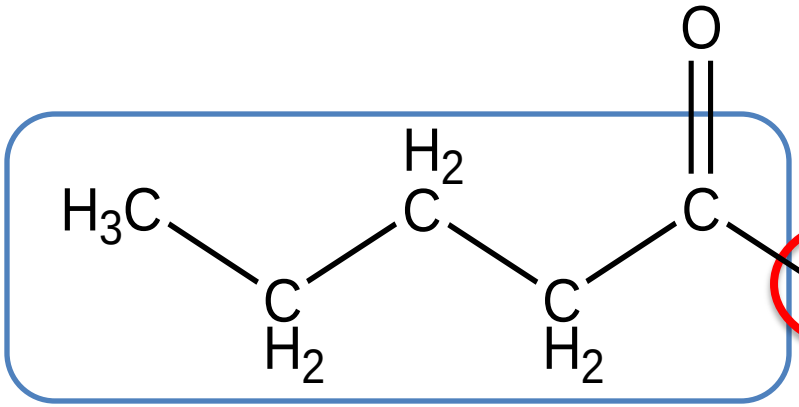
Secondary (2°) amine

N-methylpentanamide

Naming amides



5 C → pentane → pentanamide



Methyl

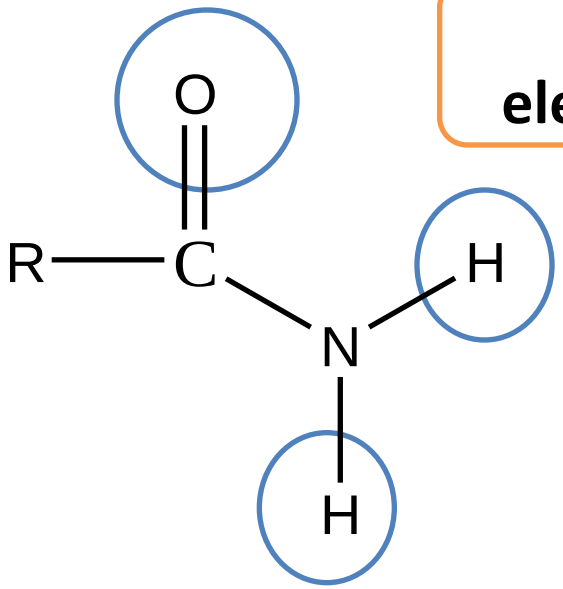
Tertiary (3°) amine

N,N-dimethylpentanamide

Methyl

Physical properties of amides

- primary amide

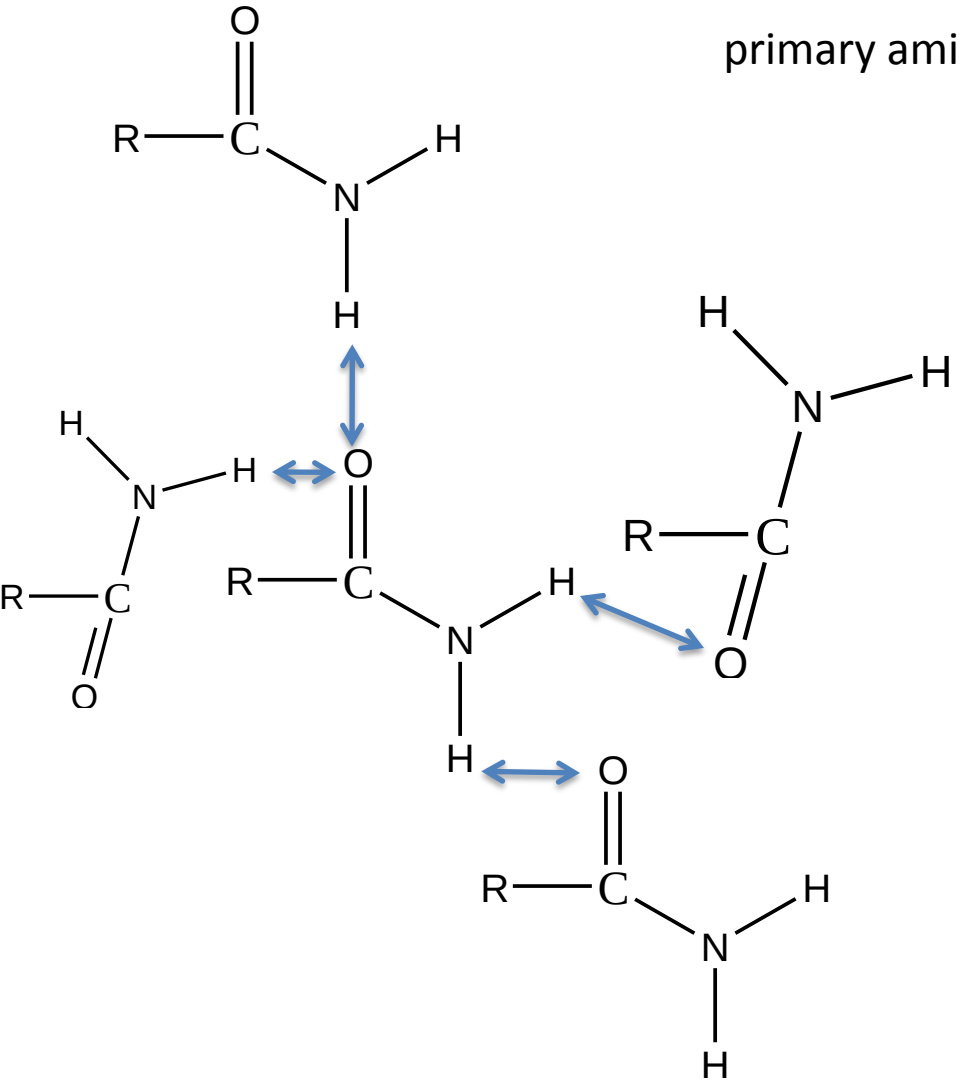


N (nitrogen) and O (oxygen)→ electronegative atom → polar molecule

Hydrogen bonding?

Physical properties of amides

primary amide

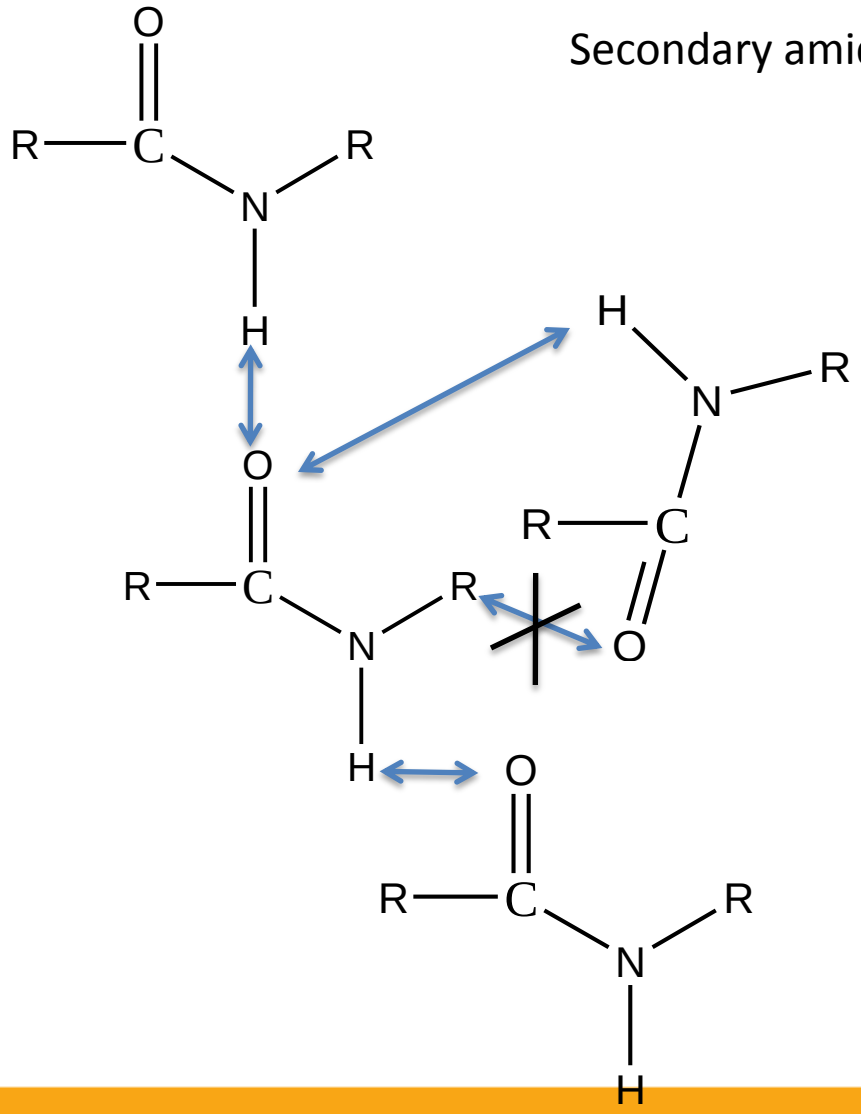


❖**Hydrogen bonding between molecules of same compound.**

❖**Up to 4 hydrogen bonds can occur for primary amide.**

Physical properties of amides

Secondary amide

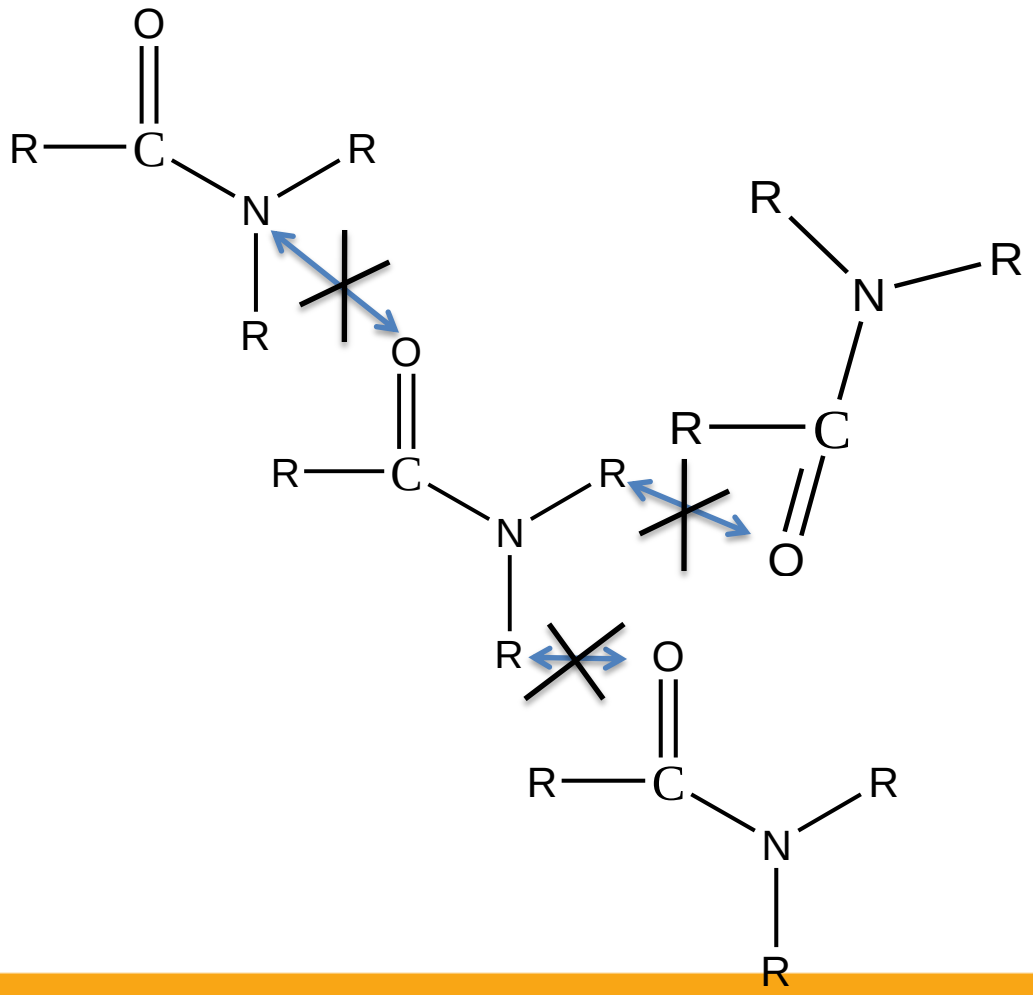


❖**Hydrogen bonding between molecules of same compound.**

❖**Up to 3 hydrogen bonds can occur for secondary amide.**

Physical properties of amides

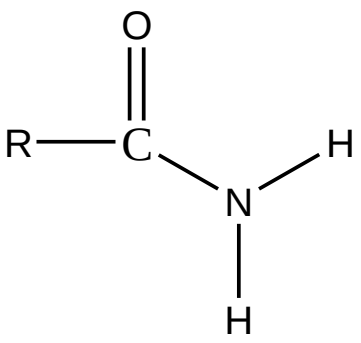
Tertiary amide

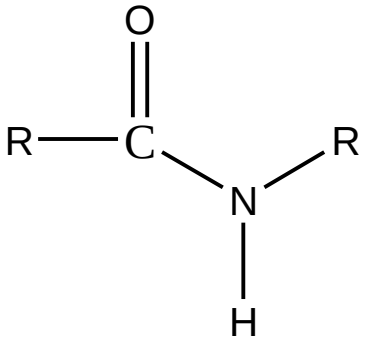


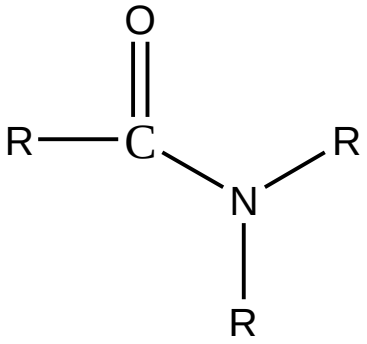
❖**No hydrogen bonding between molecules of same compound for tertiary amide.**

Physical properties of amides

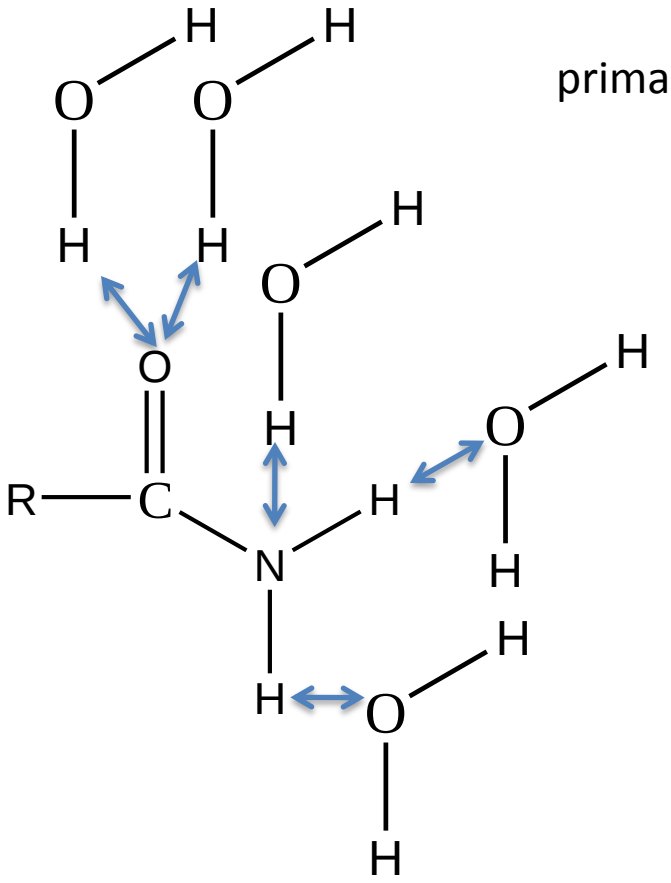
- Hydrogen bonding with water?







Physical properties of amides

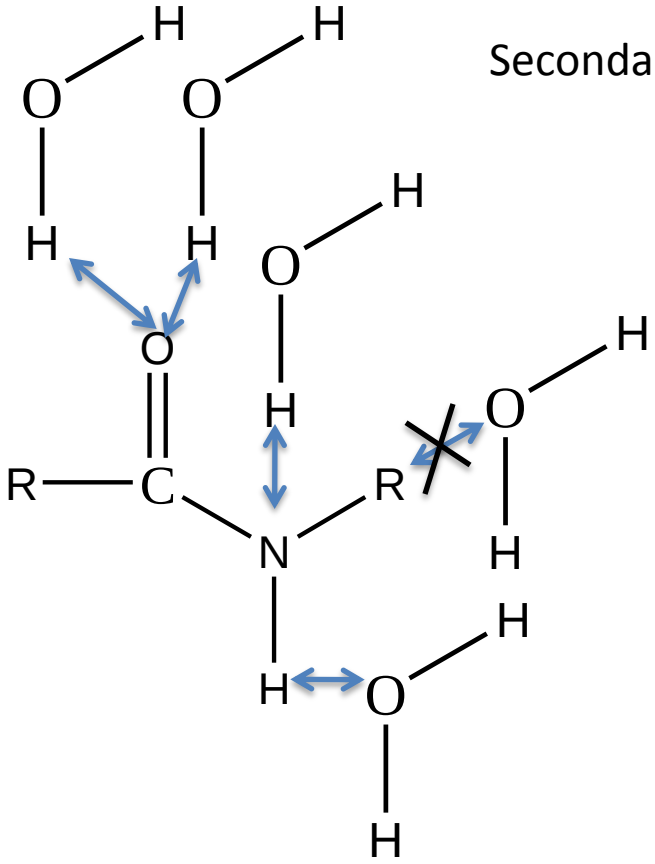


primary amide

❖**Hydrogen bonding with water.**

❖**Up to 5 hydrogen bonds can occur for primary amide.**

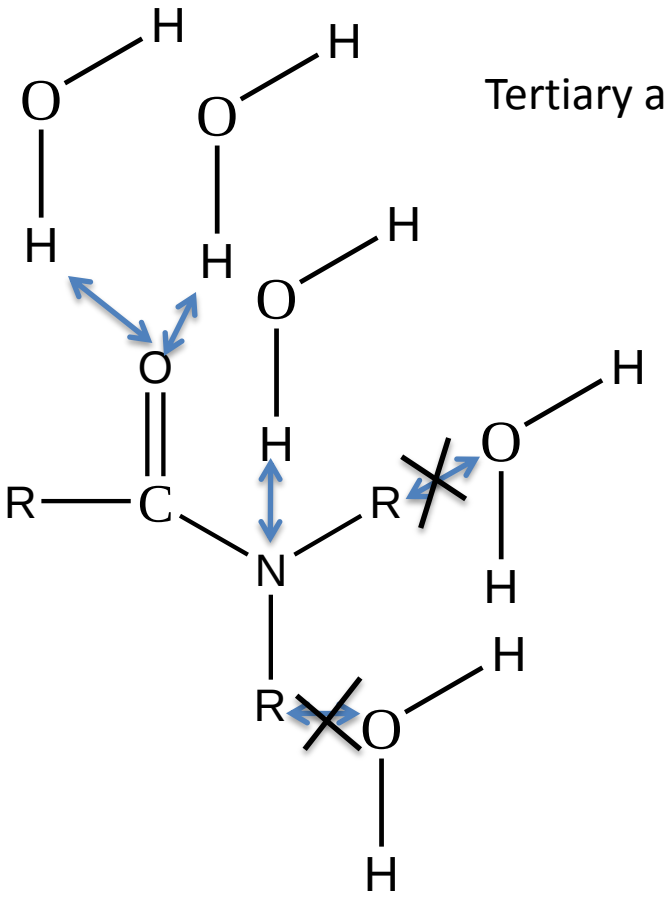
Physical properties of amides



Secondary amide

- **Hydrogen bonding with water.**
- **Up to 4 hydrogen bonds can occur for secondary amide.**

Physical properties of amides

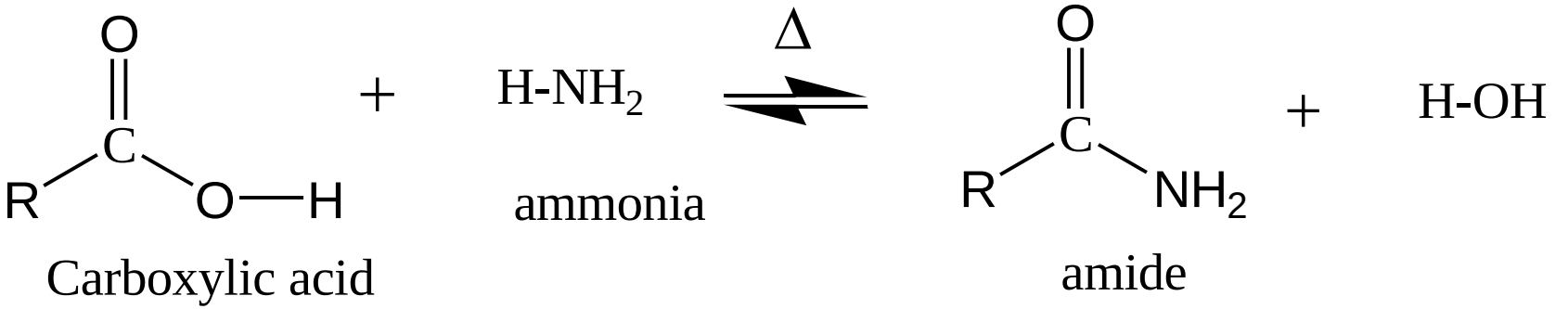


Tertiary amide

- **Hydrogen bonding with water.**
- **Up to 3 hydrogen bonds can occur for tertiary amide.**

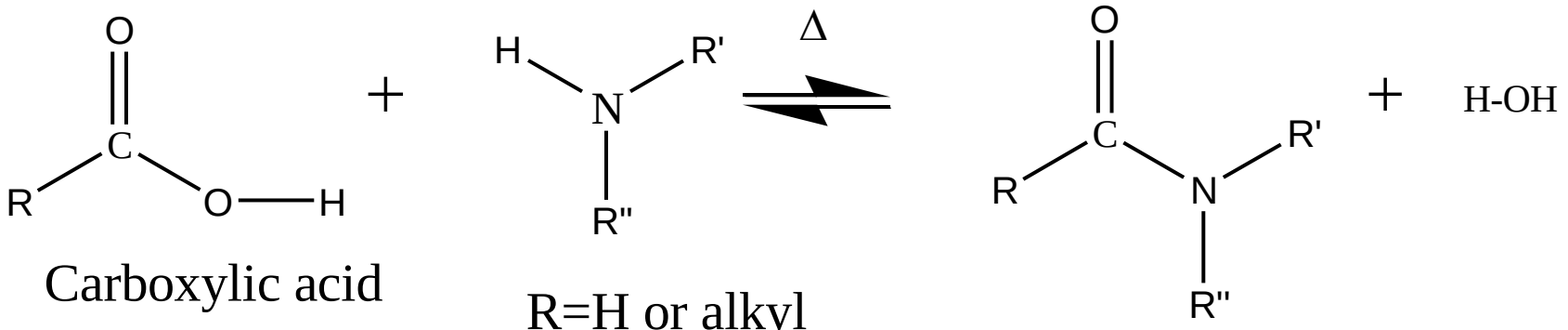
Formation of Amide

- Heating a carboxylic acid (RCOOH) with ammonia (NH_3) or an amine ($R'NH_2$ or R'_2NH) forms an amide



Carboxylic acid

amide



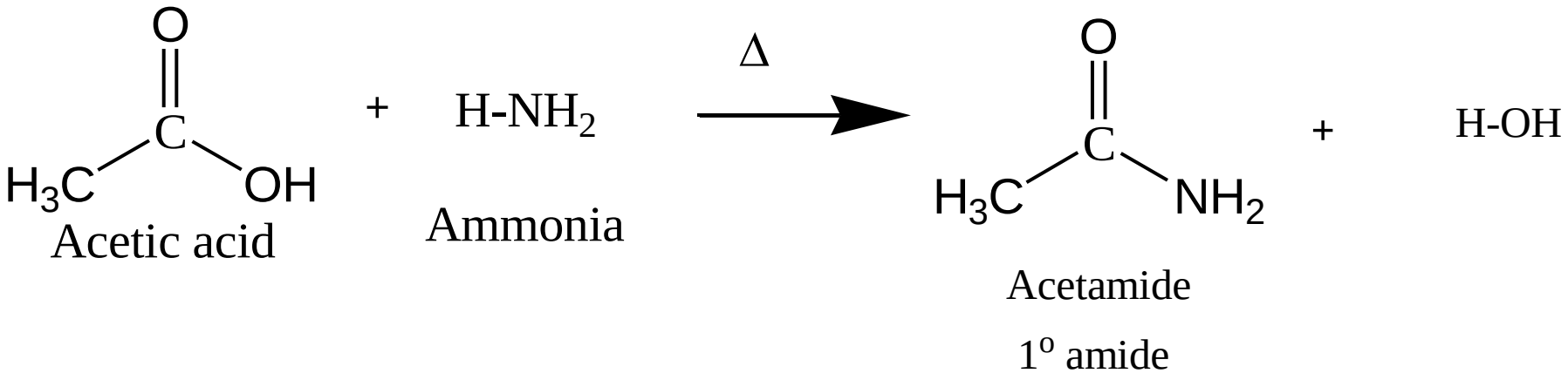
Carboxylic acid

R=H or alkyl

amide

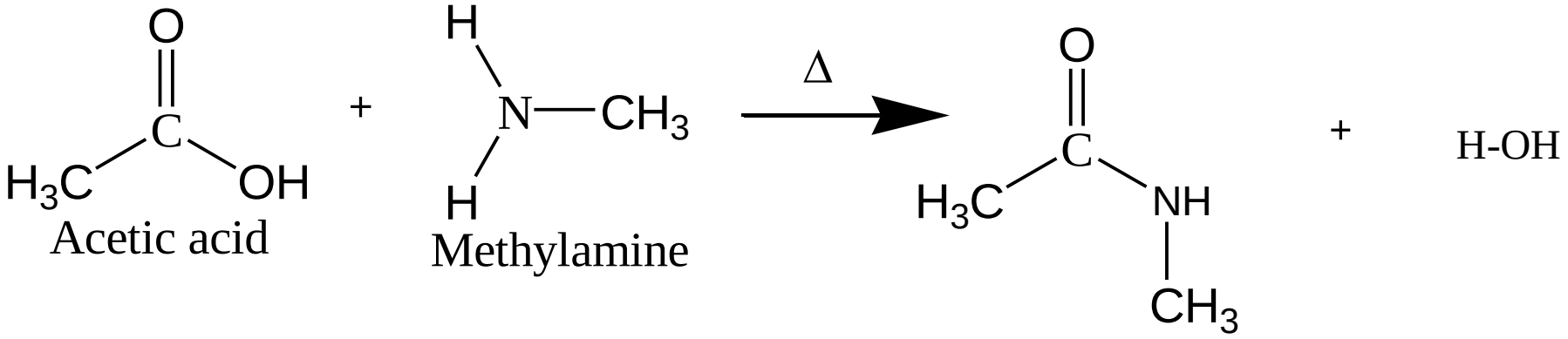
Formation of Amide

- Reaction of RCOOH with NH_3 forms a 1° amide ($RCONH_2$)



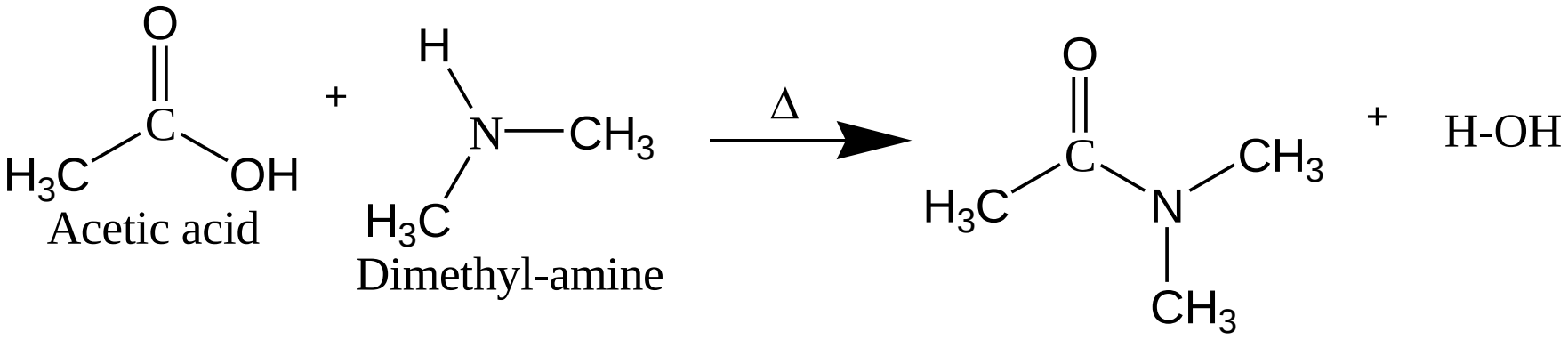
Formation of Amide

- Reaction of RCOOH with R'NH_2 forms a 2° amide (RCONHR')



Formation of Amide

- Reaction of RCOOH with R'_2NH forms a 3° amide ($RCONR'_2$)

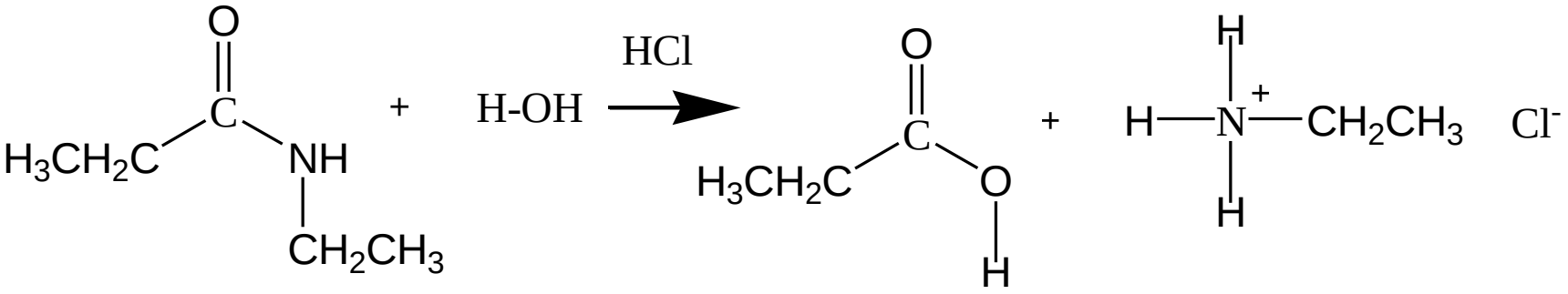


N,*N*-Dimethyl-acetamide

3^o amide

Hydrolysis of Amide

- Treatment of an amide (RCONHR') with water in the presence of an acid catalyst (HCl) forms
  - a carboxylic acid (RCOOH)
  - An amine salts



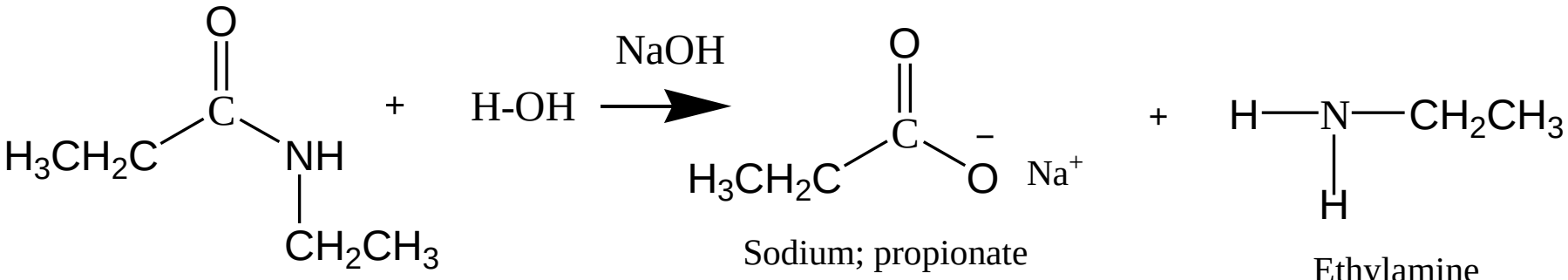
N-Ethyl-propionamide

Propionic acid

Ethyl-ammonium; chloride

Hydrolysis of Amide

- Amides are hydrolyzed in aqueous base to form
  - carboxylate anions
  - amines



N-Ethyl-propionamide

Sodium; propionate carboxylate anion

Ethylamine

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