

## CONCEPT – 05: Homologous Series

### TOPIC – 04 : Classifying molecules ; Primary, Secondary, Tertiary and Quaternary compounds

#### How To Recognize Primary, Secondary, Tertiary and sometimes Quaternary Hydrocarbons, Carbocations, Alkyl Halides, Alcohols, Amines, and Amides :

- Primary ( $1^\circ$ ), secondary ( $2^\circ$ ), tertiary ( $3^\circ$ ) and quaternary ( $4^\circ$ ) alkyl carbons are defined according to the number of carbons directly attached to that carbon.
- Similar nomenclature can be used for carbocations. Primary ( $1^\circ$ ), secondary ( $2^\circ$ ), and tertiary ( $3^\circ$ ) carbocations are defined according to the number of carbons directly attached to the carbon bearing the positive charge.
- Primary ( $1^\circ$ ), secondary ( $2^\circ$ ), and tertiary ( $3^\circ$ ) alcohols are defined according to the number of carbons directly attached to the carbon bearing the hydroxyl group.

- Primary ( $1^\circ$ ), secondary ( $2^\circ$ ), and tertiary ( $3^\circ$ ) alkyl halides are defined similarly to alcohols.
- Amines and amides are defined according to the number of carbons directly attached to the nitrogen atom.

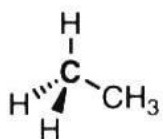
## 1. Primary, Secondary, Tertiary, and Quaternary Alkyl Hydrocarbons

There are four possible bonding patterns for alkyl carbons in hydrocarbons.

- **Primary carbons ( $1^\circ$ )** are carbons attached to one other carbon and three hydrogens. Also known as a methyl ( $\text{CH}_3$ )
- **Secondary carbons ( $2^\circ$ )** are attached to two other carbons and two hydrogens. Also known as methylene ( $\text{CH}_2$ ) carbons.
- **Tertiary carbons ( $3^\circ$ )** are attached to three other carbons and one hydrogen. Also known as methine ( $\text{R}_3\text{CH}$ ) carbons.
- Finally, **quaternary carbons ( $4^\circ$ )** are attached to four other carbons.

We can't go higher than that. To have five substituents, 10 electrons around carbon are required, a clear violation of the octet rule. Writing 5 covalent bonds around one carbon will count as a mistake.

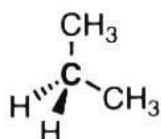
Alkyl carbons are classified as primary, secondary, tertiary or quaternary according to the number of directly attached to the carbon in question.



**Primary (1°)  
Carbon**

“methyl”

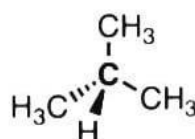
-C attached to  
One carbon



**Secondary (2°)  
Carbon**

“methylene”

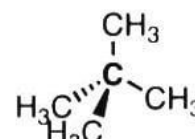
-C attached to  
two carbons



**Tertiary (3°)  
Carbon**

“methine”

-C attached to  
three carbons



**Quaternary (4°)  
Carbon**

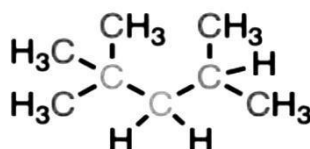
“quaternary”

-C attached to  
four carbons

**Example :**

Isooctane

1 Secondary carbon



5 Primary carbons

1 Tertiary carbon

1 Quaternary carbon

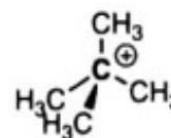
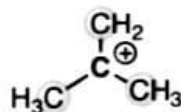
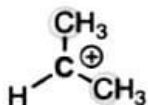
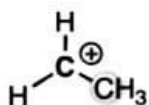
It's important to note that the terms primary, secondary, tertiary and quaternary only apply for alkyl carbons and carbocations, when the carbon participates in pi-bonding (multiple bonding such as double or triple bonding), different names are applied.

## 2. Primary, Secondary, and Tertiary Carbocations

Carbocations can also be classified as primary, secondary, or tertiary according to the number of carbons **directly attached** to the positively charged carbon.

Quaternary carbocations don't exist. The problem is that the extra p-orbital on carbon would bring the number of orbitals on carbon to 5, violating the octet rule.

**Carbocations** can also be classified as primary, secondary, or tertiary according to the number of attached carbons.



**Primary (1°)  
Carbocation**

-C attached to  
**one** carbon

**Secondary (2°)  
Carbocation**

-C attached to  
**two** carbons

**Tertiary (3°)  
Carbocation**

-C attached to  
**three** carbons

**Quaternary (4°)  
Carbocation**

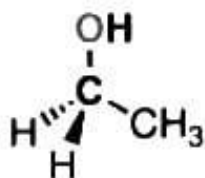
-does not exist  
-would **require 5**  
orbitals at carbon  
breaking octet rule

### 3. Primary, Secondary, and Tertiary Alcohols

Primary, secondary, and tertiary alcohols are named according to the number of carbons directly attached to the C-OH carbon. This carbon is sometimes known as the carbinol carbon.

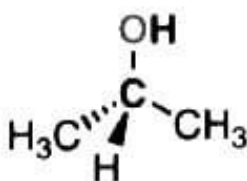
There is no such thing as a quaternary alcohol because that would require having 5 bonds to carbon.

Alcohols are classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ), or tertiary ( $3^\circ$ ) according to the number of carbons **directly attached** to the carbon bonded to the OH.



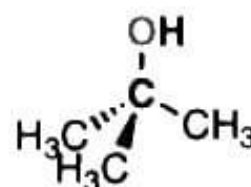
**Primary ( $1^\circ$ )  
alcohol**

-C-OH carbon  
attached to  
**one** carbon



**Secondary ( $2^\circ$ )  
alcohol**

- C-OH carbon  
attached to  
**two** carbons



**Tertiary ( $3^\circ$ )  
alcohol**

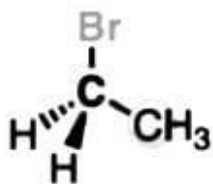
- C-OH carbon  
attached to  
**three** carbons

## 4. Primary, Secondary, and Tertiary Alkyl Halides

Alkyl halides have an  $sp^3$  hybridized carbon directly attached to a halogen.

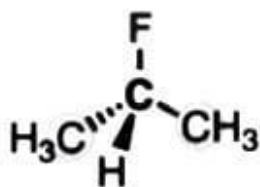
Like alcohols, they are named according to the number of carbons directly attached to the carbon containing the halogen.

**Alkyl halides are** classified as primary, secondary, or tertiary according to the number of carbons **directly attached** to the carbon bonded to the halogen.



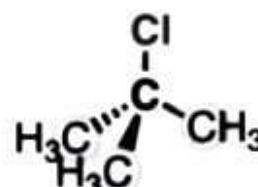
**Primary**  
**Alkyl halide ( $1^\circ$ )**

-C-OH carbon  
attached to  
**one** carbon



**Secondary**  
**Alkyl halide ( $2^\circ$ )**

- C-OH carbon  
attached to  
**two** carbon



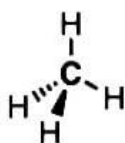
**Tertiary**  
**Alkyl halide ( $3^\circ$ )**

- C-OH carbon  
attached to  
**three** carbon

## 5. A Special Case: Methane and Methyl Groups

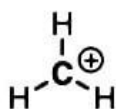
Up to this point we've left out the special case of methane, the only hydrocarbon which lacks any carbon-carbon bonds.

### The Special case of methane



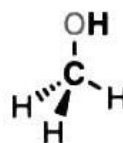
**Methane**

-C attached to  
0 carbon,  
4 hydrogens



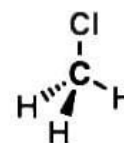
**Methyl  
Carbocation**

-C attached to  
0 carbon,  
3 hydrogens



**Methyl  
alcohol**

-C attached to  
0 carbon,  
3 hydrogens

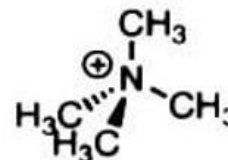
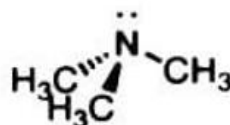
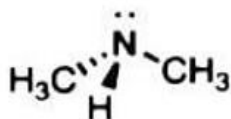
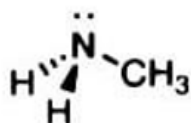


**Methyl  
halide**

-C attached to  
0 carbon,  
3 hydrogens

## 6. Primary, Secondary, and Tertiary Amines and Quaternary Ammonium Salts

Next, we come to amines, Amines are named according to the number of carbons attached to the **nitrogen**. **Primary, secondary, and tertiary** amines are nitrogen bound to **one, two** and **three** carbons, respectively. It is possible for the nitrogen to be bound to a fourth carbon. This species is known as an **alkylammonium salt**. It is not technically an amine since it lacks a lone pair on nitrogen and cannot act as a base.



**Primary (1°)  
amine**

**Secondary (2°)  
amine**

**Tertiary(3°)  
amine**

**Quaternary (4°)  
amine**

-N attached to  
**one** carbon

-N attached to  
**two** carbons

-N attached to  
**three** carbons

-N attached to  
**four** carbons

Remember that the positive formal charge on nitrogen doesn't imply that there is an empty p orbital there. Always assume a full octet on positively charged nitrogen and oxygen.