3.3: ALKYL GROUPS

OBJECTIVES

After completing this section, you should be able to

1. recognize and name any alkyl group that can be considered to have been formed by the removal of a terminal hydrogen atom from a straight-chain alkane containing ten or fewer carbon atoms.
2. explain what is meant by a primary, secondary, tertiary or quaternary carbon atom.
3. represent the various types of organic compounds using the symbol “R” to represent any alkyl group.

KEY TERMS

Make certain that you can define, and use in context, the key terms below.

- alkyl group
- methyl group
- isopropyl group
- *sec*-butyl group
- isobutyl group
- *tert*-butyl group
- primary carbon
- secondary carbon
- tertiary carbon
- quaternary carbon

STUDY NOTES

The differences among primary, secondary, tertiary and quaternary carbon atoms are explained in the following discussion. A convenient way of memorizing this classification scheme is to remember that a primary carbon atom is attached directly to only one other carbon atom, a secondary carbon atom is attached directly to two carbon atoms, and so on.

The **IUPAC** system requires first that we have names for simple unbranched chains and second, that we have names for simple alkyl groups that may be attached to the chains. An **alkyl group** is formed by removing one hydrogen from the alkane chain. The removal of this hydrogen results in a stem change from **-ane** to **-yl** to indicate an alkyl group. The removal of a hydrogen from methane, CH_4, creates a methyl group $-CH_3$. Likewise, the removal of a hydrogen from ethane, CH_3CH_3, creates an ethyl group $-CH_2CH_3$. The nomenclature pattern can continue to provide a series of straight-chain alkyl groups from straight chain alkanes with a hydrogen removed from the end. Note, the letter **R** is used to designate a generic (unspecified) alkyl group.

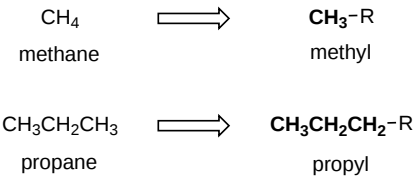


Table 3.3.2: Straight chain alkane and alkyl group names

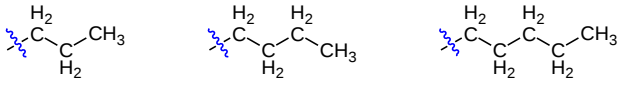
Alkane	Name	Alkyl Group	Name (Abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl
$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	$-CH_2CH_2CH_2CH_2CH_2CH_3$	Hexyl

Prior to the systematic nomenclature developed for organic chemistry, prefixes were used to specify the connection point of straight-chain and branched-chain alkyl groups. Although the modern nomenclature system, discussed in the next section, is preferred these older terms are still often used, especially in solvents and reagents. Thus, an understanding of these prefixes is important to understanding organic

chemistry. Notice that the total number of carbons in the alkyl subsistent is still indicated with the **prefix + yl**. For methyl and ethyl alkyl groups there is only one possible connection point so connection prefixes are not necessary. Starting with a three carbon alkyl group (propyl) the possibility of multiple connection points necessitates connection prefixes. These prefixes are often abbreviated with a letter which is italicized.

NORMAL (*N*)

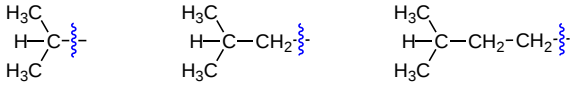
The prefix "n" is used to indicate a connection at the end of a straight-chain alkane. This prefix is not commonly used to just indicate alkyl subsistent as discussed above. However it is sometime used to indicate the connection of a functional group onto a straight alkane.



n-propyl or propyl | *n*-butyl or butyl | *n*-pentyl or pentyl

ISO (*I*)

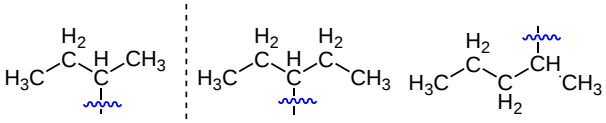
Starting with propyl alkyl groups there is the possibility of a connection other than the very end. The prefix "iso" implies that the connection ends with a $(CH_3)_2CH$- group.



isopropyl or *i*-propyl | isobutyl or *i*-butyl | isopentyl or *i*-pentyl

SECONDARY (*SEC*)

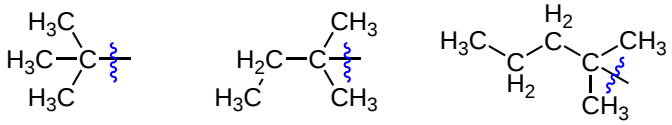
With butyl straight-chain alkyl groups there is the possibility of a connection on the second carbon from the end of the chain. These alkyl groups are given the prefix "*Sec.*" This is not used for pentyl or hexyl groups because there is more than one structure that are not identical that could be named as sec-pentyl or sec-hexyl.



sec -butyl | NOT *sec* -pentyl

TERTIARY (*TERT* OR *T*)

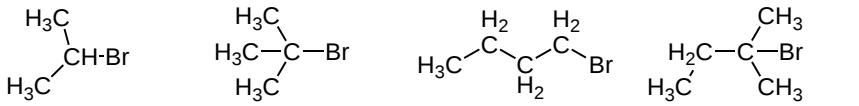
Starting with four carbon alkyl groups, there is an isomer which can have a connection to a tertiary carbon. These alkyl groups get the prefix "*t.*"



tert-butyl or *t*-butyl | *tert*-pentyl or *t*-pentyl | *tert*-hexyl or *t*-hexyl

EXAMPLE:

The naming system described above is often used to describe halogens which contain only a few carbons. The halogen is shown as bonded to the connection point of the alkyl group.



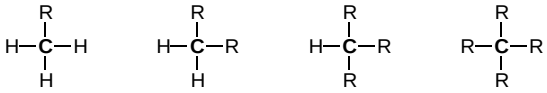
isopropyl bromide | *t*-butyl bromide | *n*-butyl bromide | *tert*-pentyl bromide

CLASSIFICATION OF CARBON ATOMS

Carbons have a special terminology to describe how many other carbons they are attached to. This allows for an easy description of branching in alkanes. Also, we will find that the number of carbons attached to a given atom will have subtle effects on its chemistry.

- Primary carbons (1°) attached to one other C atom.
- Secondary carbons (2°) are attached to two other C's.
- Tertiary carbons (3°) are attached to three other C's.
- Quaternary carbons (4°) are attached to four C's.

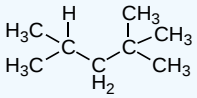
The figure below use the group "R" to represent an alkyl group of unspecified length. R typically used to represent alkyl groups but an also represent a part of a molecule which is either unspecified or not germane to the discussion.



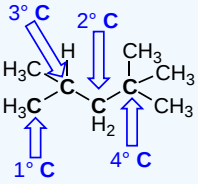
This terminology will be used repeatedly in organic chemistry to describe the number of carbons attached to a specific atom, however, the atom will not always a carbon.

EXAMPLE 3.3.1

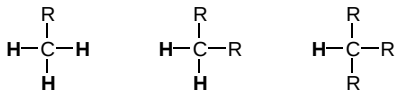
Please indicate the the number of 1°, 2°, 3°, and 4° carbons in the following molecule:



- The molecule has five Primary carbons (1°).
- The molecule has one Secondary carbon (2°).
- The molecule has one Tertiary carbon (3°).
- The molecule has one Quaternary carbon (4°)



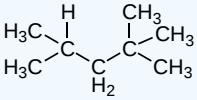
Hydrogen atoms are also classified in this manner. A hydrogen atom attached to a primary carbon atom is called a primary hydrogen ect.



- Primary hydrogens (1°) are attached to carbons bonded to one other C atom
- Secondary hydrogens (2°) are attached to carbons bonded to two other C's
- Tertiary hydrogens (3°) are attached to carbons bonded to three other C's
- It is not possible to have a quaternary hydrogen (4°).

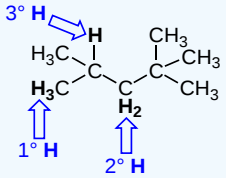
EXAMPLE 3.3.2

Please indicate the the number of 1°, 2°, and 3°, hydrogens are in the following molecule:



- The molecule has fifteen Primary (1°) hydrogens.

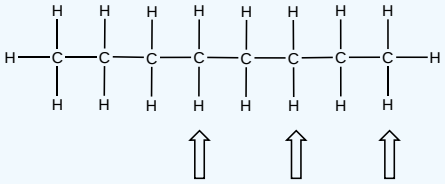
- The molecule has two Secondary (2°) hydrogens.
- The molecule has one Tertiary (3°) hydrogen.



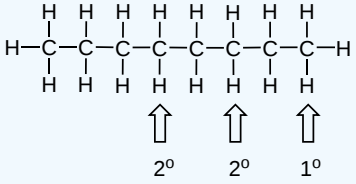
EXERCISES

EXERCISE 3.3.1

Determine whether the H's indicated in the following structure are 1°, 2°, or 3°.

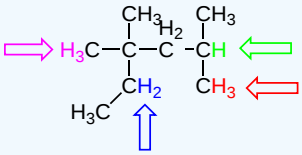


Answer

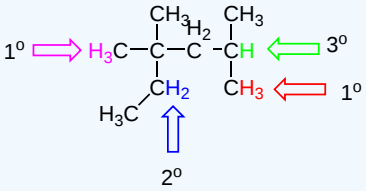


EXERCISE 3.3.2

Determine whether the H's indicated in the following structure is 1°, 2°, or 3°.

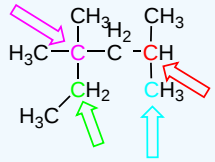


Answer

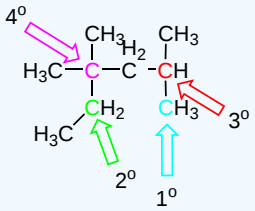


EXERCISE 3.3.3

Determine whether the carbons indicated in the structure below are 1°, 2°, 3°, or 4°.

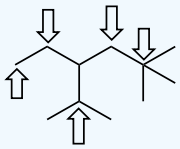


Answer

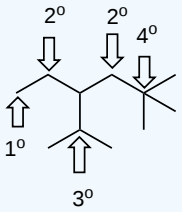


EXERCISE 3.3.4

Determine whether the carbons indicated in the structure below are 1°, 2°, 3°, or 4°.

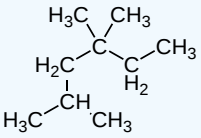


Answer



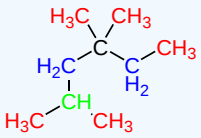
EXERCISE 3.3.5

Please indicate the total number of each type 1°, 2°, 3°, and 4° carbons in the following molecule.



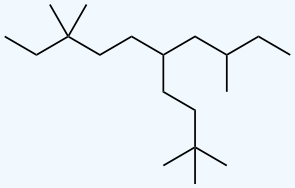
Answer

There are 5 primary (1°) C's, 2 secondary (2°) C's, 1 tertiary (3°) C and 1 quaternary (4°) C in the structure (seen color coded below).



EXERCISE 3.3.6

Please indicate the total number of each type 1^o, 2^o, 3^o, and 4^o carbons in the following molecule.



Answer

There are 8 primary (1^o) C's, 7 secondary (2^o) C's, 2 tertiary (3^o) C's and 2 quaternary (4^o) C's in the structure (seen color coded below).