

CHAPTER 5

FUNCTIONAL GROUPS AND NOMENCLATURE I

Functional group

A group of atoms where the reaction takes place

Nomenclature

Systematic method for naming

5.1 Alkanes \Rightarrow Saturated hydrocarbons

Hydrocarbon means a organic compound containing only C and H.

Then alkanes have all single bonds

Ex) (linear) alkanes, C_nH_{2n+2} , $DU=0$

cycloalkanes, C_nH_{2n} , $DU=1$ (but *no* multiple bonds)

Properties and applications of Hydrocarbon

⇒ H and C have close electronegativity values, 2.1 and 2.5.

1. Insignificant bond dipoles
2. Nonpolar compound
3. London forces only (low mp and bp)
4. hydrophobic (*not* hydrophilic) and floats on water (why?)

Alkane is also called as paraffin (from the Latin for 'little affinity')

Strong C-H & C-C bonds and $pK_a = 40\sim 50$

⇒ The most important use of alkanes; fuel (see p.146 for E content)

⇒ Chemists use alkanes as solvents for nonpolar compounds

occurrence: natural gas, petroleum & coal

⇒ Purification by distillation, cracking & reforming

5.2 Common Nomenclature of Alkanes

In the earlier days organic chemistry, nomenclature of compounds were not systematic,

then you should memorize all of them

Ex) butyrum is the Latin word for butter

The acid from rancid butter is butyric acid, then four carbon alkane is butane.

Then straight butane is normal butane and branched butane is isobutane

5.3 Systematic Nomenclature of Alkanes

IUPAC (International Union of Pure and Applied Chemistry)
nomenclature

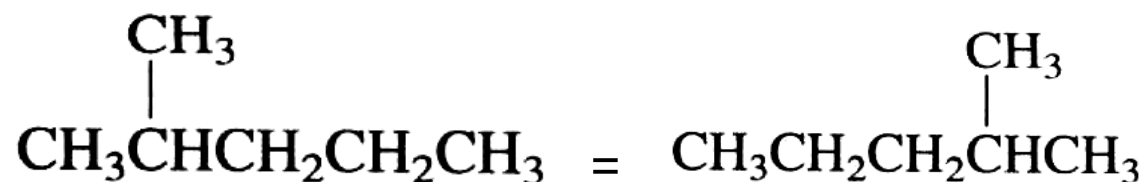
How to name an alkane

longest continuous carbon chain

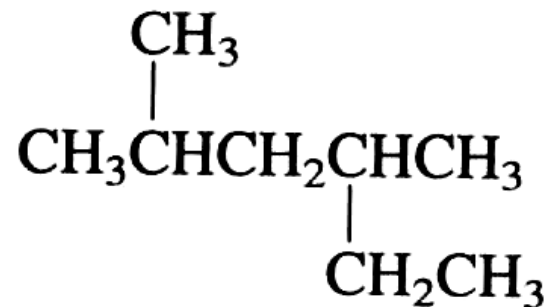
ROOT

When equal length, greater number of branches

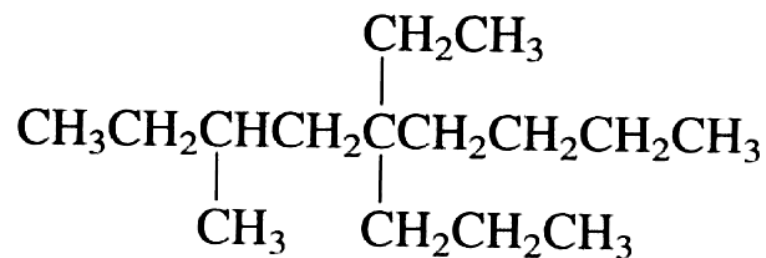
Examples)



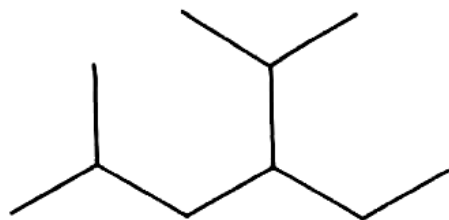
2-methylpentane



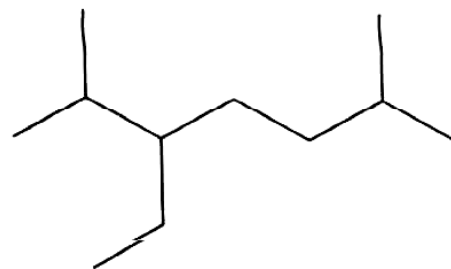
2,4-methylhexane



5-ethyl-3-methyl-5-propylnonane



3-ethyl-2,5-dimethylhexane



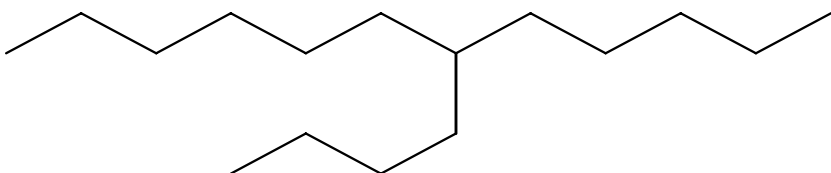
3-ethyl-2,6-dimethylheptane

Naming complex branches

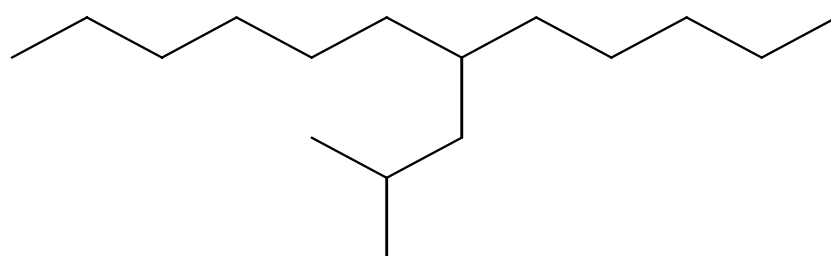
1. Find the longest chain beginning at the branch. propyl
2. Number from the branching point. 2-methylpropyl
3. Put the complex group in parentheses: (2-methylpentyl)

Additional terminology

Examples of butyl branches

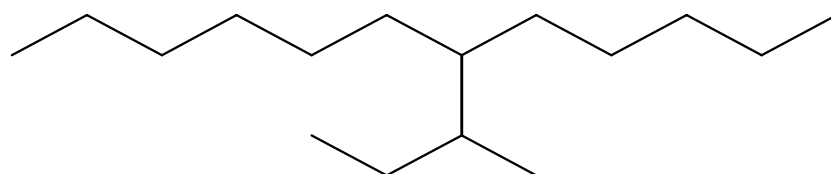


6-(*n*-)butyldodecane



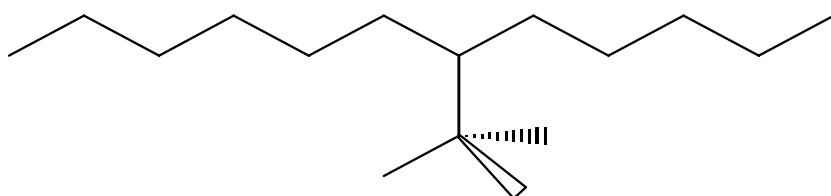
6-(2-methylpropyl)dodecane

6-isobutyldodecane



6-(1-methylpropyl)dodecane

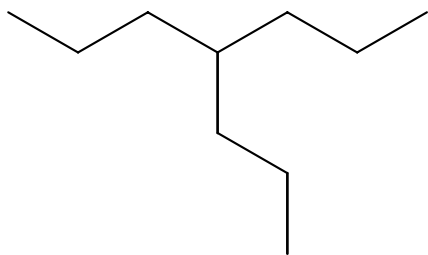
6-*sec*-butyldodecane



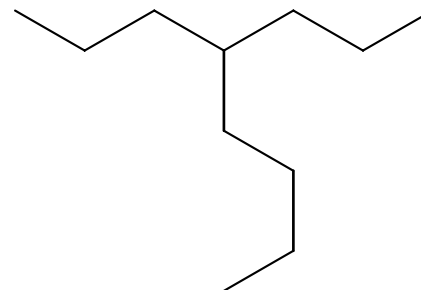
6-(1,1-dimethylethyl)dodecane

6-*tert*-butyldodecane

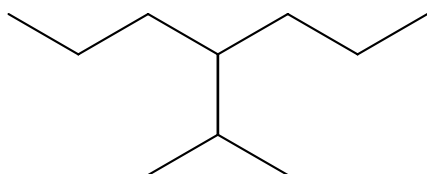
Common name for branches



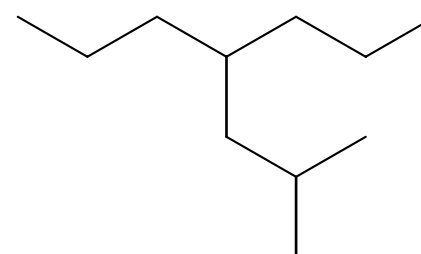
*(n-)*propyl



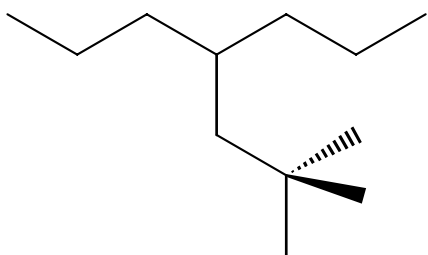
*(n-)*butyl



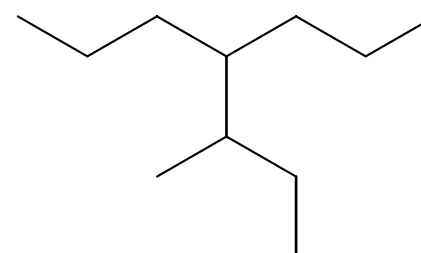
isopropyl



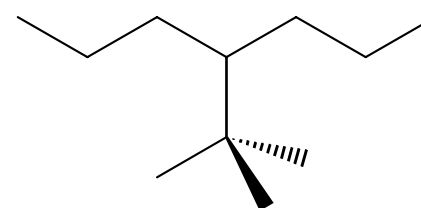
isobutyl



neopentyl



*sec-*butyl



*tert-*butyl
*t-*butyl

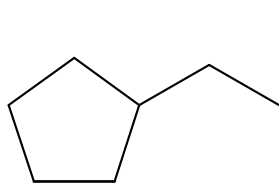
5.4 Nomenclature of cycloalkane

Similar to that used for alkane except using a prefix of cyclo

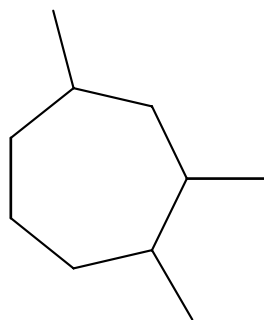
⇒ prefix+cyclo+root+ane

Rules

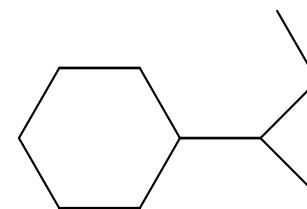
1. No number is needed if only one group is attached
2. When there are multiple substituent, keep the numbers as low as possible
 - ❖ Lower position number for substituents; prefix



ethylcyclopentane

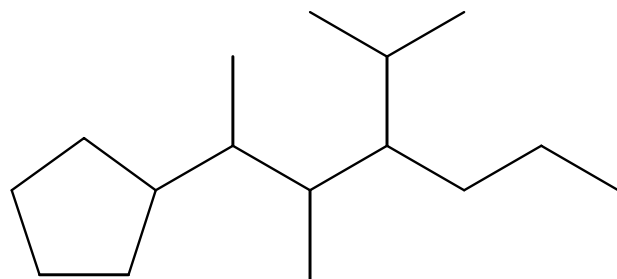


1,2,4-trimethylcycloheptane
Not 1, 3,4 or 1,5,7



(1-methylpropyl)cyclohexane
sec-butylcyclohexane

If the substituent has more carbons than the ring has,
then the ring is a substituent group (cycloalkyl-)



2-cyclopentyl-3-methyl-4-(1-methylethyl)-heptane

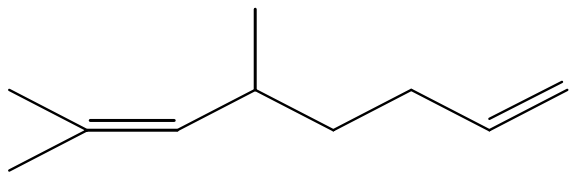
2-cyclopentyl-4-isopropyl-3-methylheptane

5.5 Alkenes

⇒ Unsaturated HC with one or more C=C double bonds

Nomenclature; Similar to alkanes

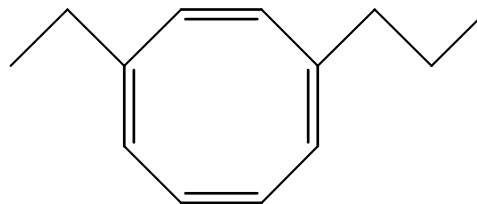
1. Choose longest chain with double bond
2. suffix. -ene (one double bond), -diene (two =), -triene (three =), ...
3. Numbering starts from the end that gives the lower number to the first carbon of the double bond



octadiene

2,4-dimethyl-2,7-octadiene (X)

5,7-dimethyl-1,6-octadiene



cyclooctatetraene

1-ethyl-6-propyl-1,3,5,7-cyclooctatetraene

—

Physical property

nonpolar polar; think of dipole moment \Rightarrow physical properties similar to alkanes

ex) 1-pentene; bp = 30 °C, mp = - 138 °C

pentane; bp = 36 °C, mp = - 130 °C

Chemical property

Double bonds are more reactive (ΔE of pi bonding = ~ 64 kcal/mol)
than single bonds (ΔE of sigma bonding = ~90 kcal/mol)

Unsaturated fat reacts (is oxidized) easier than saturated fat.

In nature

Ethene; plant hormone that causes ripening in fruit

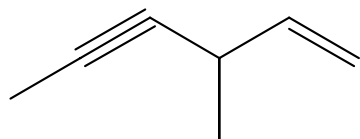
limonene; in citrus fruit

β -carotene; orange pigment in carrot

5.6 Alkynes

Unsaturated hydrocarbon with one or more $C\equiv C$ triple bonds

Nomenclature is same to alkenes except that the suffix is yne



hexen-yne

3-methyl-1-hexen-4-yne

3-methylhex-1-en-4-yne

Physical properties of alkane, alkene, and alkyne are close

Ex) hexane; bp = 69 °C

1-hexene; bp = 63 °C

1-hexyne; bp = 71 °C

Chemical property of Alkyne is close to alkene; alkyne have two pi bond to be reacted, while alkene has only one.

Rarely occur in nature

5.7 Alkyl Halides (Haloalkanes)

Compounds with one or more halogens in place of hydrogen

Nomenclature is same as alkane with a halogen as a substituent
(halo- (IUPAC) or - halide (common))



| | | | |
|----|----------|---------|----------|
| F | fluorine | fluoro- | fluoride |
| Cl | chlorine | chloro- | chloride |
| Br | bromine | bromo- | bromide |
| I | iodine | iodo- | iodide |

Properties

1. C-X bond slightly polar

1-chlororbutane (MW = 92.5 g/mol); bp = 78 °C

Hexane (MW = 86 g/mol);; bp = 69 °C

2. Immiscible with water and sink beneath

3. Relatively stable; can be used as solvents, flame retardants, coolant.

See p 162

5.8 Alcohols

Compound with hydroxy (OH) group

Nomenclature: suffix of -ol (IUPAC) or groupyl alcohol (trivial)

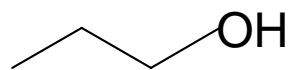
Priority of functional groups 492 Table 12.3

□ Properties

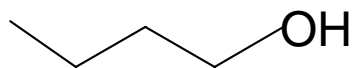
Higher mp due to polarity of hydroxy group

Higher bp due to H-bonding

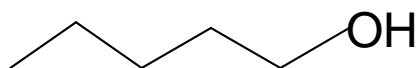
Hydroxy group is hydrophilic



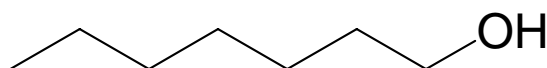
soluble in (miscible with) water



2.7 g is soluble in 100 mL of water

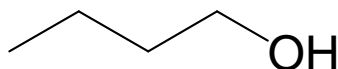


0.9 g is soluble in 100 mL of water

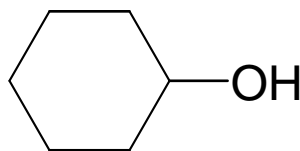


insoluble in (immiscible with) water

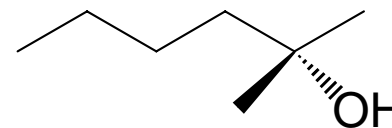
□ Reactivity depends on steric effect



primary (1°)

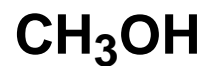


secondary (2°)



tertiary (3°) alcohol

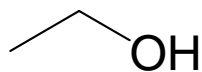
□ Occur in nature or from petrochemicals



methanol

methyl alcohol

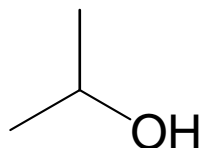
MeOH



ethanol

ethyl alcohol

EtOH



2-propanol

isopropyl alcohol

i-PrOH (IPA)

Menthol is a [covalent organic compound made synthetically](#) or obtained from [peppermint](#) or other [mint](#) oils. It is a waxy, crystalline substance, clear or white in color, which is solid at [room temperature](#) and melts slightly above. The main form of menthol occurring in nature is (–)-menthol, which is assigned the (1*R*,2*S*,5*R*) [configuration](#). Menthol has [local anesthetic](#) and counterirritant qualities, and it is widely used to relieve minor throat irritation.

History and occurrence

Shimoyama has asserted[1] that menthol has been known in Japan for more than 2000 years, but in the west it was not isolated until 1771, by Gambius.[3] (–)-Menthol (also called *l*-menthol or (1*R*,2*S*,5*R*)-menthol) occurs naturally in peppermint oil (along with a little [menthone](#), the ester [menthyl acetate](#) and other compounds), obtained from *mentha x piperita*. Japanese menthol also contains a small percentage of the 1-[epimer](#), (+)-neomenthol.

[\[edit\]](#)

Structure

Natural menthol exists as one pure [enantiomer](#), nearly always the (1*R*,2*S*,5*R*) form (bottom left of diagram below). The other seven [stereoisomers](#) are:

In the natural compound, the [isopropyl](#) group is oriented [trans](#)- orientation to both the [methyl](#) and [alcohol](#) groups. Thus it can be drawn in any of the ways shown:

In the ground state all three bulky groups in the chair are [equatorial](#), making (–)-menthol and its enantiomer the most stable two isomers out of the eight.

There are two crystal forms for racemic menthol; these have melting points of 28 °C and 38 °C. Pure (–)-menthol has four crystal forms, of which the most stable is the α form, the familiar broad needles.

[\[edit\]](#)

- ❑ Applications
- ❑ Menthol is contained in non-prescription products for short-term relief of minor sore throat and minor mouth or throat irritation, for example in [lip balms](#) and [cough medicines](#). It is classed as an [antipruritic](#), which reduces itching. Menthol is also contained in combination products used for relief of muscle aches, sprains, and similar conditions, as well as in [decongestants](#). In addition, it is used as an additive in certain [cigarette](#) brands, both for flavor and to reduce the throat and sinus irritation caused by smoking. Menthol is a common ingredient in [mouthwash](#).
- ❑ Some supporters of the [homeopathic](#) theory of [pharmacology](#), which is not accepted by most licensed physicians, believe that menthol interferes with the effects of homeopathic remedies, and they strongly discourage its use for those seeking homeopathic cures -- to the point of prohibiting use of mint flavored toothpaste. Currently no other reported nutrient or herb interactions involve menthol. Menthol is available as a dietary supplement or natural medicine in the form of peppermint oil. It is used in Eastern medicine to treat indigestion, nausea, sore throat, diarrhoea, colds, and headaches. (-)-Menthol has low toxicity: Oral (rat) [LD50](#): 3300 mg/kg; Skin (rabbit) [LD50](#): 15800 mg/kg).
- ❑ Menthol is used to prepare menthyl esters, for example [menthyl acetate](#), used in [perfumery](#) to emphasise floral notes (especially rose).
- ❑ In [organic chemistry](#), menthol is used as a [chiral auxiliary](#) in [asymmetric synthesis](#). For example, [sulfinates esters](#) made from [sulfinyl chlorides](#) and menthol can be used to make [enantiomerically pure sulfoxides](#) by reaction with [organolithium reagents](#) or [Grignard reagents](#). Menthol is also used for [classical resolution](#) of chiral carboxylic acids, via the menthyl esters.
- ❑ [\[edit\]](#)
- ❑ "

5.9 Ethers

Compound with two hydrocarbon bonded to one Oxygen

Nomenclature

1. alkyl alkyl ether (common)
2. Small alkyl + oxygen ; alkoxy- (IUPAC)

For some reasons common names are used more oftenly



Alphabetic order, c first

Properties

low mp and bp

a little polar C-O, but *no* H-bonding betw themselves

partially soluble in water (comparable to ROH)

H-bonding with water

Useful for p. 174

❖ anesthetic $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ diethyl ether 'ether'

❖ solvent

not very reactive -- stable

not very polar -- dissolve organics

Lewis base -- interact with cation -- dissolve salts

not (protonic) acidic -- esp useful for strong bases

'ether', petroleum ether, DME, THF, 1,4-dioxane

5.10 Amines

Derivatives of ammonia (NH_3)

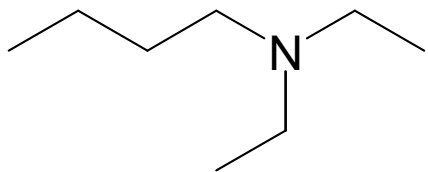
primary (1°) amine ; one H of ammonia replaced by alkyl

Secondary (2°) amine ; two Hs of ammonia replaced by alkyl

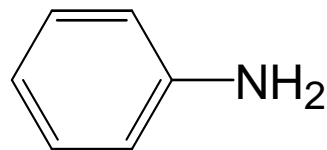
Tertiary (3°) amine ; three Hs of ammonia replaced by alkyl

Quaternary (4°) ammonium salt; four alkyl groups

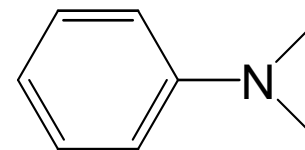
Nomenclature, common: --amine



N,N-diethylbutylamine

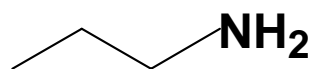


aniline

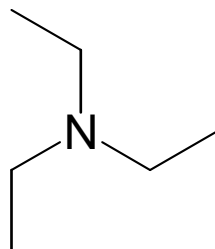


N,N-dimethylaniline

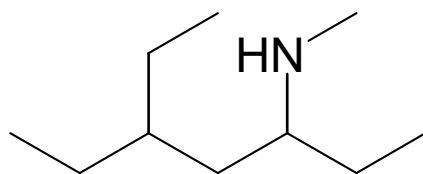
Nomenclature, IUPAC: similar to alcohol



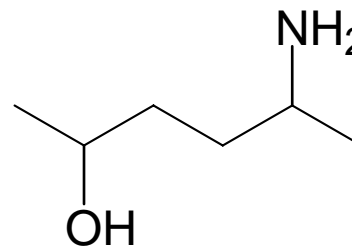
propylamine
propanamine



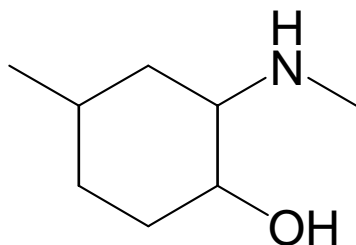
triethylamine
N,N-diethylethanamine



5-ethyl-N-methyl-3-heptanamine



5-amino-2-hexanol



2-methylamino-4-methylcyclohexanol

Properties

1° (RNH₂) and 2° (RNHR') amine

polar and H-bonding – similar to ROH

H-bonding weaker than ROH

mp and bp; RH < RNH₂ < ROH

Ex) pentane; bp= 36 °C

butylamine; bp= 78 °C

1-butanol; bp= 117 °C

3° amine (RR'R''N)

✓ no H-bonding -- properties similar to ROR'

Odor; ammonialike or fishy odor

Alkaloids ; natural amines occur in plants

Why Alkaloids ? Because they are basic and extracted from plants using aqueous acid as shown in the following reaction.

Relative strength of H-bonding