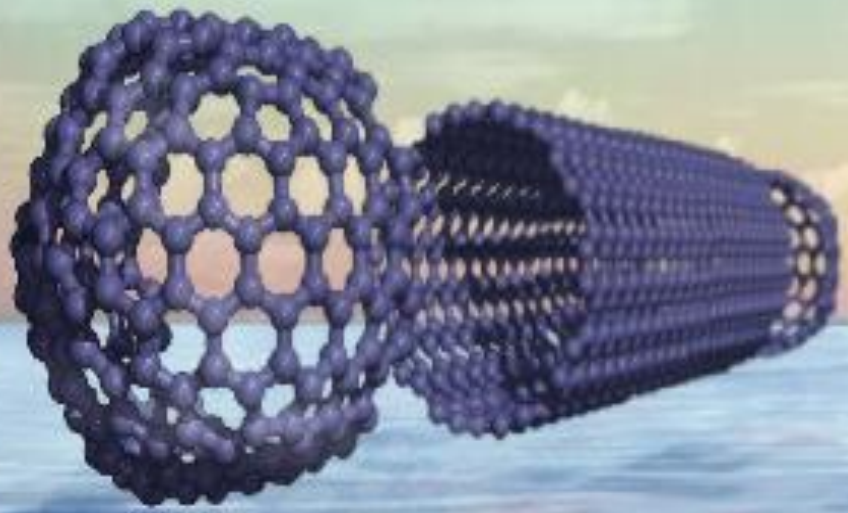
جامعة الملك سعود
King Saud University

Organic Chemistry



By
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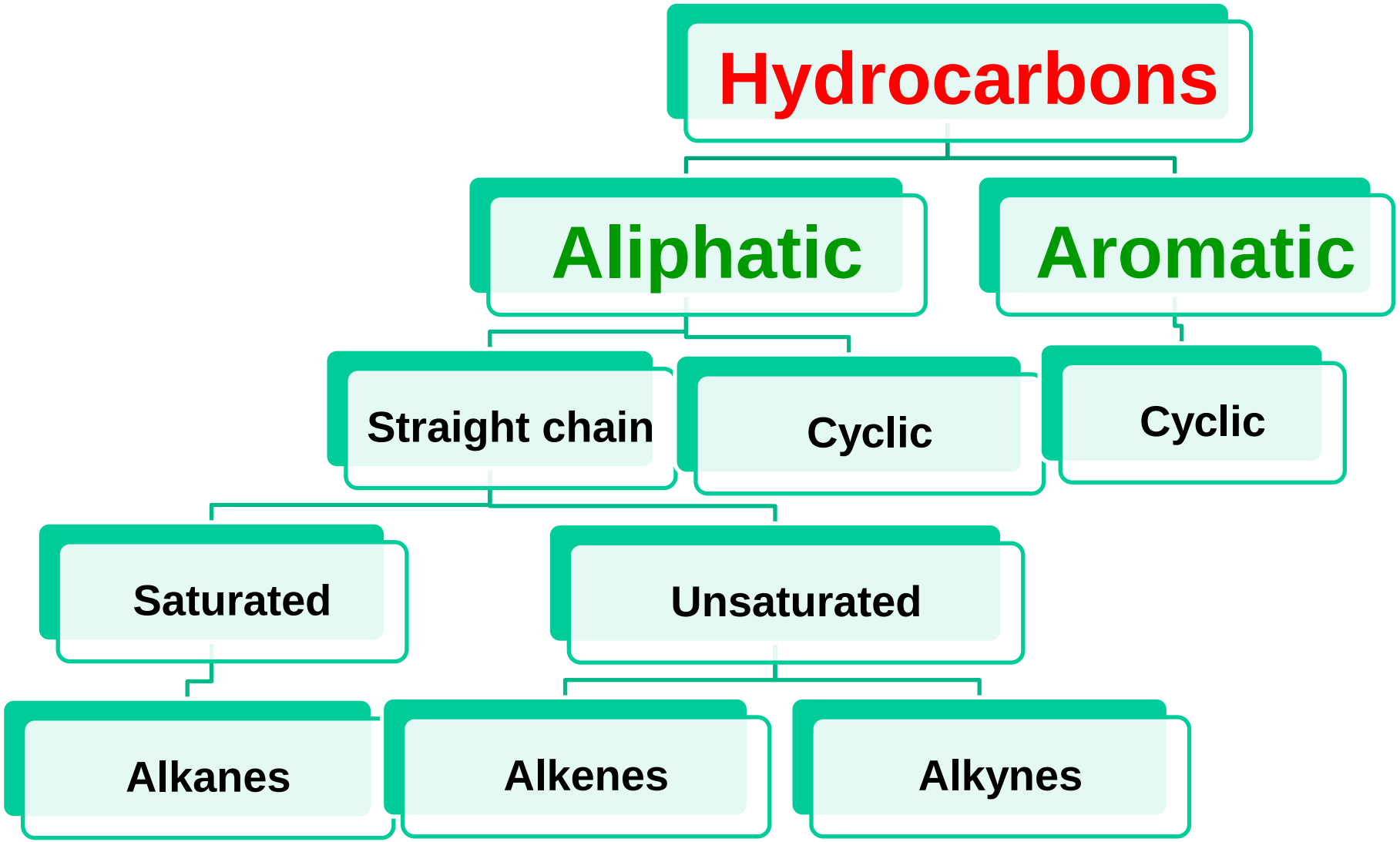
Hydrocarbons

Dr. Assem Barakat


Hydrocarbons
Aliphatic
Aromatic
Straight chain
Cyclic
Cyclic
Saturated
Unsaturated
Alkanes
Alkenes
Alkynes

1. **Hydrocarbons:**

1) **Alkanes:** C_nH_{2n+2} (saturated)

i) **Cycloalkanes:** C_nH_{2n} (containing a single ring)

ii) Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.

2) **Alkenes:** C_nH_{2n} (containing one double bond)

3) **Alkynes:** C_nH_{2n-2} (containing one triple bond)

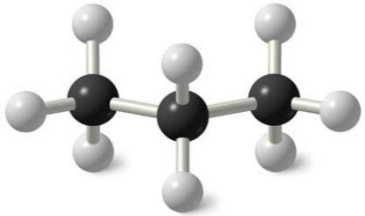
Alkanes

Open-chain alkanes (without rings) all have the general formula C_nH_{2n+2}, where *n* equals the number of carbon atoms. The following table shows the structures and names for the first 10 unbranched, open-chain alkanes. Look at the trends in the boiling and melting points and the density of the alkanes as their mass increases.

♦ Shapes of Alkanes

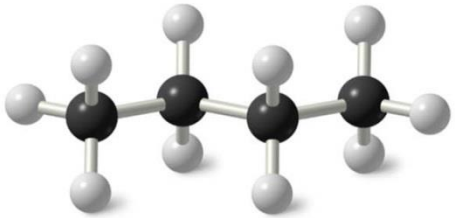
➔ **"Straight-chain" alkanes have a zig-zag orientation when they are in their most straight orientation**

- **Straight chain alkanes are also called unbranched alkanes**



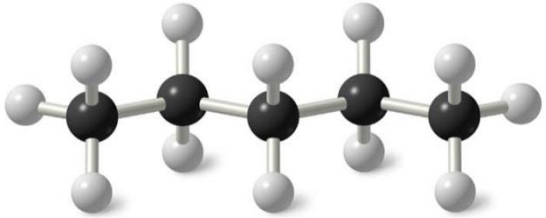
Propane

$CH_3CH_2CH_3$ or 



Butane

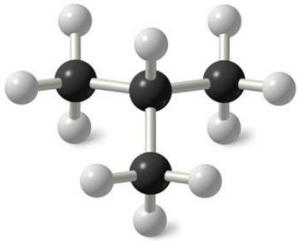
$CH_3CH_2CH_2CH_3$ or 



Pentane

$CH_3CH_2CH_2CH_2CH_3$ or 

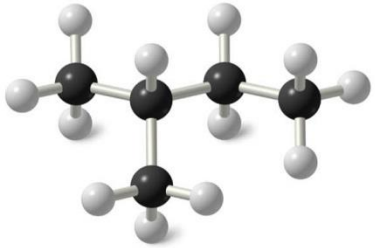
➔ **Branched alkanes have at least one carbon which is attached to more than two other carbons**



Isobutane

CH_3CHCH_3 or

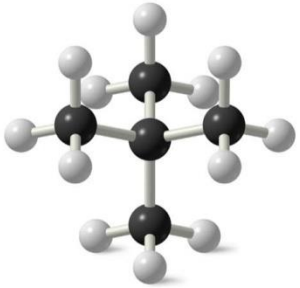
CH_3



Isopentane

$CH_3CHCH_2CH_3$ or

CH_3



Neopentane

CH_3

CH_3CCH_3 or

CH_3

➔ **Constitutional isomers have different physical properties (melting point, boiling point, densities etc.)**

- **Constitutional isomers have the same molecular formula but different connectivity of atoms**

Molecular Formula	Structural Formula	mp (°C)	bp (°C)[a] (1 atm)	Density[b] (g mL^{-1})	Index of Refraction[c] (n_D 20°C)
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	−95	68.7	0.6594^{20}	1.3748
C_6H_{14}	$CH_3CH(CH_3)CH_2CH_2CH_3$	−153.7	60.3	0.6532^{20}	1.3714
C_6H_{14}	$CH_3CH_2CH(CH_3)CH_2CH_3$	−118	63.3	0.6643^{20}	1.3765
C_6H_{14}	$CH_3CH(CH_3)CH(CH_3)CH_3$	−128.8	58	0.6616^{20}	1.3750
C_6H_{14}	$CH_3C(CH_3)_2CH_2CH_3$	−98	49.7	0.6492^{20}	1.3688

[a] Unless otherwise indicated, all boiling points given in this book are at 1 atm or 760 torr.
[b] The superscript indicates the temperature at which the density was measured.
[c] The index of refraction is a measure of the ability of the alkane to bend (refract) light rays. The values reported are for light of the D line of the sodium spectrum (n_D).

➔ **The number of constitutional isomers possible for a given molecular formula increases rapidly with the number of carbons**

Molecular Formula	Possible Number of Constitutional Isomers
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763
$C_{40}H_{82}$	62,481,801,147,341

♦ IUPAC Nomenclature of Alkanes

- ➔ Before the end of the 19th century compounds were named using nonsystematic nomenclature
- ➔ These “common” or “trivial” names were often based on the source of the compound or a physical property
- ➔ The International Union of Pure and Applied Chemistry (IUPAC) started devising a systematic approach to nomenclature in 1892
- ➔ The fundamental principle in devising the system was that each different compound should have a unique unambiguous name
- ➔ The basis for all IUPAC nomenclature is the set of rules used for naming alkanes

- **Nomenclature of Unbranched Alkanes**

Name	Number of Carbon Atoms	Structure	Name	Number of Carbon Atoms	Structure
Methane	1	CH_4	Heptadecane	17	$CH_3(CH_2)_{15}CH_3$
Ethane	2	CH_3CH_3	Octadecane	18	$CH_3(CH_2)_{16}CH_3$
Propane	3	$CH_3CH_2CH_3$	Nonadecane	19	$CH_3(CH_2)_{17}CH_3$
Butane	4	$CH_3(CH_2)_2CH_3$	Eicosane	20	$CH_3(CH_2)_{18}CH_3$
Pentane	5	$CH_3(CH_2)_3CH_3$	Heneicosane	21	$CH_3(CH_2)_{19}CH_3$
Hexane	6	$CH_3(CH_2)_4CH_3$	Docosane	22	$CH_3(CH_2)_{20}CH_3$
Heptane	7	$CH_3(CH_2)_5CH_3$	Tricosane	23	$CH_3(CH_2)_{21}CH_3$
Octane	8	$CH_3(CH_2)_6CH_3$	Triacontane	30	$CH_3(CH_2)_{28}CH_3$
Nonane	9	$CH_3(CH_2)_7CH_3$	Hentriacontane	31	$CH_3(CH_2)_{29}CH_3$
Decane	10	$CH_3(CH_2)_8CH_3$	Tetracontane	40	$CH_3(CH_2)_{38}CH_3$
Undecane	11	$CH_3(CH_2)_9CH_3$	Pentacontane	50	$CH_3(CH_2)_{48}CH_3$
Dodecane	12	$CH_3(CH_2)_{10}CH_3$	Hexacontane	60	$CH_3(CH_2)_{58}CH_3$
Tridecane	13	$CH_3(CH_2)_{11}CH_3$	Heptacontane	70	$CH_3(CH_2)_{68}CH_3$
Tetradecane	14	$CH_3(CH_2)_{12}CH_3$	Octacontane	80	$CH_3(CH_2)_{78}CH_3$
Pentadecane	15	$CH_3(CH_2)_{13}CH_3$	Nonacontane	90	$CH_3(CH_2)_{88}CH_3$
Hexadecane	16	$CH_3(CH_2)_{14}CH_3$	Hectane	100	$CH_3(CH_2)_{98}CH_3$

- **Nomenclature of Unbranched Alkyl groups**
  - ➔ **The unbranched alkyl groups are obtained by removing one hydrogen from the alkane and named by replacing the -ane of the corresponding alkane with -yl**

ALKANE		ALKYL GROUP	ABBREVIATION
CH_3—**H** **Methane**	becomes	CH_3— **Methyl**	Me—
CH_3CH_2—**H** **Ethane**	becomes	CH_3CH_2— **Ethyl**	Et—
$CH_3CH_2CH_2$—**H** **Propane**	becomes	$CH_3CH_2CH_2$— **Propyl**	Pr—
$CH_3CH_2CH_2CH_2$—**H** **Butane**	becomes	$CH_3CH_2CH_2CH_2$— **Butyl**	Bu—

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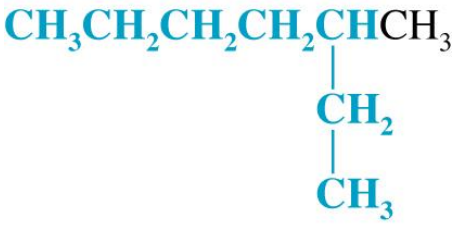
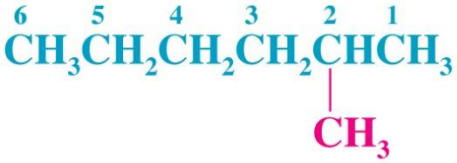
$CH_3CH_2—H$ **Ethane**	becomes	$CH_3CH_2—$ **Ethyl**	Et—
$CH_3CH_2CH_2—H$ **Propane**	becomes	$CH_3CH_2CH_2—$ **Propyl**	Pr—
$CH_3CH_2CH_2CH_2—H$ **Butane**	becomes	$CH_3CH_2CH_2CH_2—$ **Butyl**	Bu—

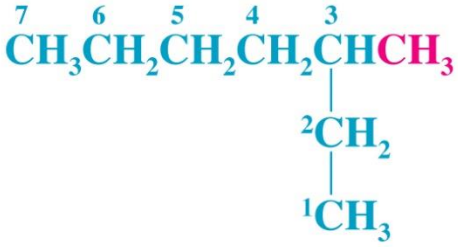
- **Nomenclature of Branched-Chain Alkanes (IUPAC)**
  - ➔ **Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name.**



  - ➔ **Number the longest chain beginning with the end of the chain nearer the substituent**
  - ➔ **Designate the location of the substituent**



2-Methylhexane



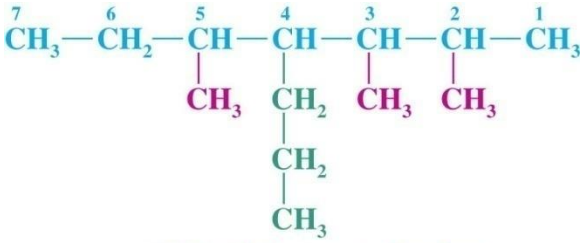
3-Methylheptane

  - ➔ **When two or more substituents are present, give each substituent a number corresponding to its location on the longest chain**
    - **Substituents are listed alphabetically**

➔ **When two or more substituents are identical, use the prefixes *di-*, *tri-*, *tetra-* etc.**

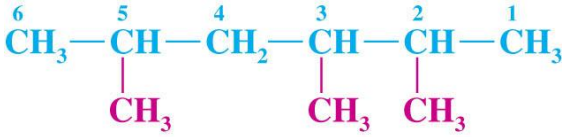
- **Commas are used to separate numbers from each other**
- **The prefixes are used in alphabetical prioritization**

➔ **When two chains of equal length compete to be parent, choose the chain with the greatest number of substituents**



2,3,5-Trimethyl-4-propylheptane
(four substituents)

➔ **When branching first occurs at an equal distance from either end of the parent chain, choose the name that gives the lower number at the first point of difference**

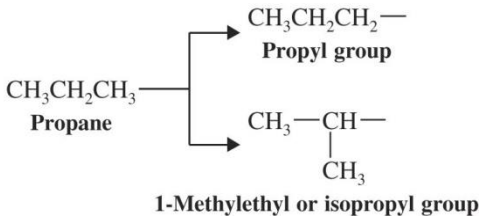


2,3,5-Trimethylhexane
(*not* 2,4,5-trimethylhexane)

- **Nomenclature of Branched Alkyl Chains**

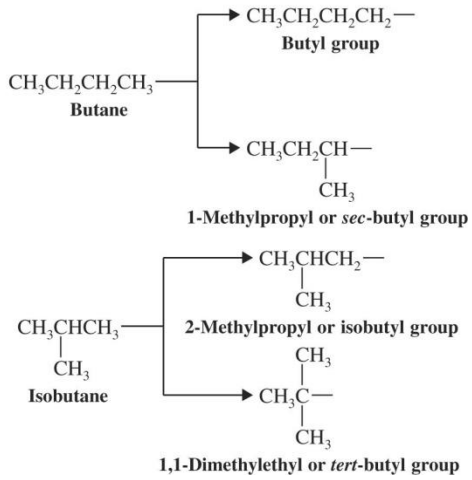
➔Two alkyl groups can be derived from propane

Three-Carbon Groups

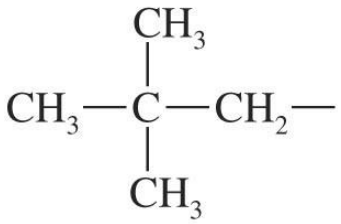


➔Four groups can be derived from the butane isomers

Four-Carbon Groups

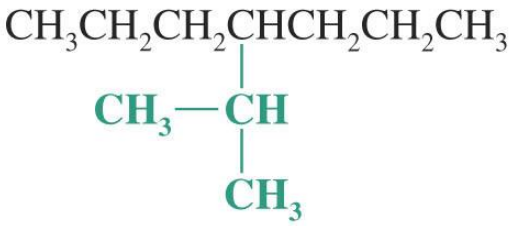


➔ **The neopentyl group is a common branched alkyl group**

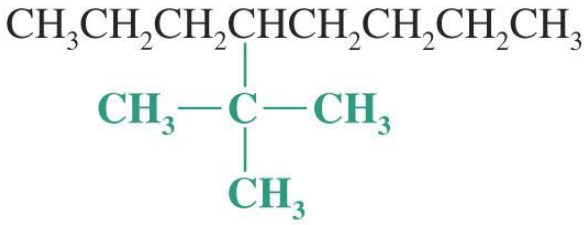


2,2-Dimethylpropyl or neopentyl group

➔ **Examples**



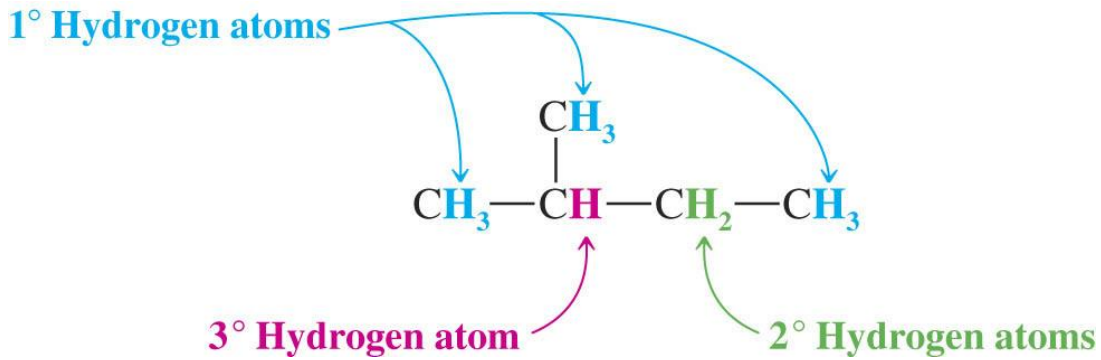
4-(1-Methylethyl)heptane or 4-isopropylheptane



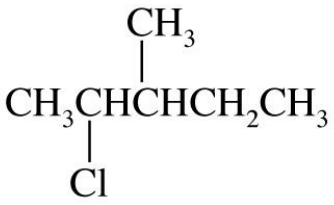
4-(1,1-Dimethylethyl)octane or 4-*tert*-butyloctane

♦ Classification of Hydrogen Atoms

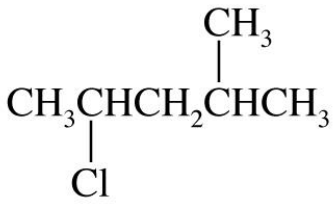
➔ **Hydrogens take their classification from the carbon they are attached to**



- **Nomenclature of Alkyl Halides**
  - ➔ **In IUPAC nomenclature halides are named as substituents on the parent chain**
    - **Halo and alkyl substituents are considered to be of equal ranking**



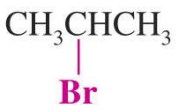
2-Chloro-3-methylpentane



2-Chloro-4-methylpentane

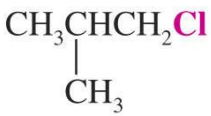
  - ➔ **In common nomenclature the simple haloalkanes are named as alkyl halides**
    - **Common nomenclature of simple alkyl halides is accepted by IUPAC and still used**

Ethyl chloride

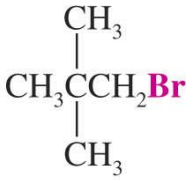


Isopropyl bromide

***tert*-Butyl bromide**

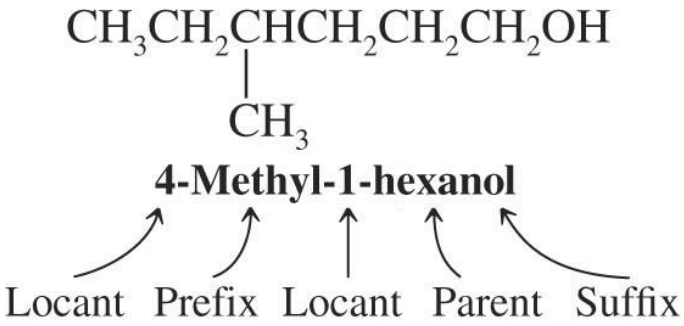


Isobutyl chloride



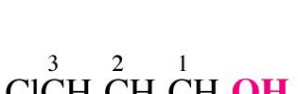
Neopentyl bromide

- **IUPAC Substitutive Nomenclature**
  - ➔ **An IUPAC name may have up to 4 features: locants, prefixes, parent compound and suffixes**
  - ➔ **Numbering generally starts from the end of the chain which is closest to the group named in the suffix**

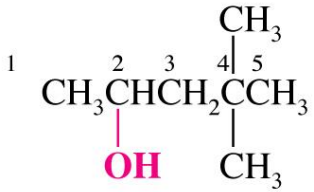


- **IUPAC Nomenclature of Alcohols**
  - ➔ **Select the longest chain containing the hydroxyl and change the suffix name of the corresponding parent alkane from -ane to -ol**
  - ➔ **Number the parent to give the hydroxyl the lowest possible number**
  - ➔ **The other substituents take their locations accordingly**

➔ **Examples**



3-Chloro-1-propanol
or 3-chloropropan-1-ol

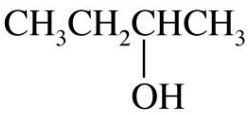


4,4-Dimethyl-2-pentanol
or 4,4-dimethylpentan-2-ol

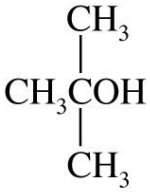
➔ **Common Names of simple alcohols are still often used and are approved by IUPAC**

Propyl alcohol

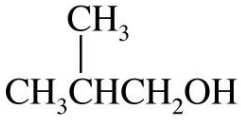
Butyl alcohol



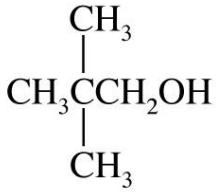
***sec*-Butyl alcohol**



***tert*-Butyl alcohol**

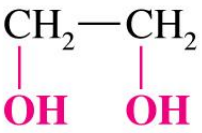
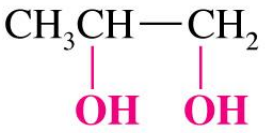
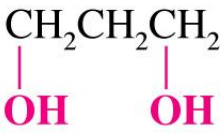


Isobutyl alcohol



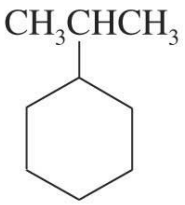
Neopentyl alcohol

➔ **Alcohols with two hydroxyls are called diols in IUPAC nomenclature and glycols in common nomenclature**

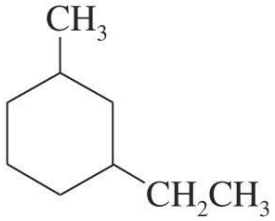
			
Common	**Ethylene glycol**	**Propylene glycol**	**Trimethylene glycol**
Substitutive	**1,2-Ethanediol or ethane-1,2-diol**	**1,2-Propanediol or propane-1,2-diol**	**1,3-Propanediol or propane-1,3-diol**

♦ Nomenclature of Cycloalkanes

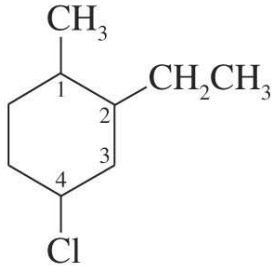
- **The prefix cyclo- is added to the name of the alkane with the same number of carbons**
  - ➔ **When one substituent is present it is assumed to be at position one and is not numbered**
  - ➔ **When two alkyl substituents are present the one with alphabetical priority is given position 1**
  - ➔ **Numbering continues to give the other substituent the lowest number**
  - ➔ **Hydroxyl has higher priority than alkyl and is given position 1**
  - ➔ **If a long chain is attached to a ring with fewer carbons, the cycloalkane is considered the substituent**



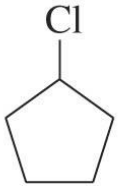
Isopropylcyclohexane



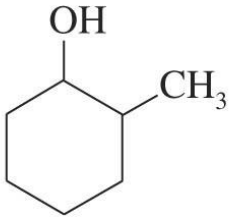
1-Ethyl-3-methylcyclohexane
(*not* 1-ethyl-5-methylcyclohexane)



4-Chloro-2-ethyl-1-methylcyclohexane
(*not* 1-chloro-3-ethyl-4-methylcyclohexane)

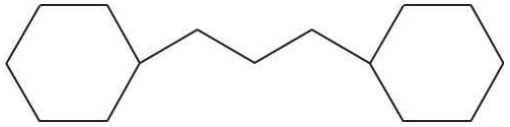


Chlorocyclopentane



2-Methylcyclohexanol

1-Cyclobutylpentane

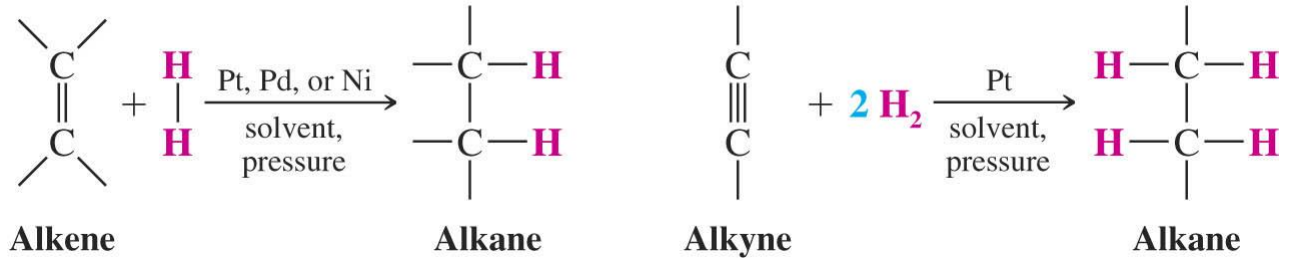


1,3-Dicyclohexylpropane

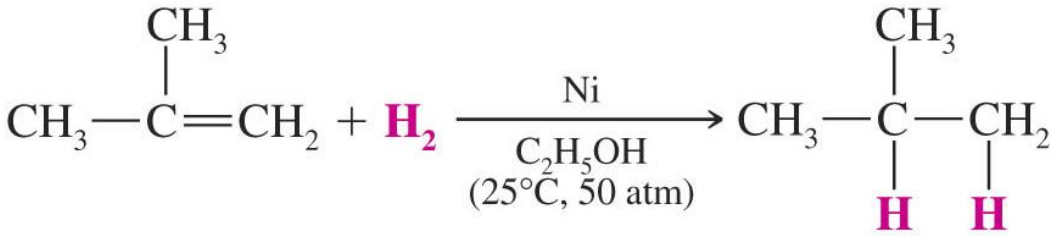
♦ Synthesis of Alkanes and Cycloalkanes

● Hydrogenation of Alkenes and Alkynes

General Reaction



Alkene **Alkane** **Alkyne** **Alkane**



2-Methylpropene **Isobutane**

- **Reduction of Alkyl Halides**

$$R{-}X + Zn + HX \longrightarrow R{-}H + ZnX_2$$

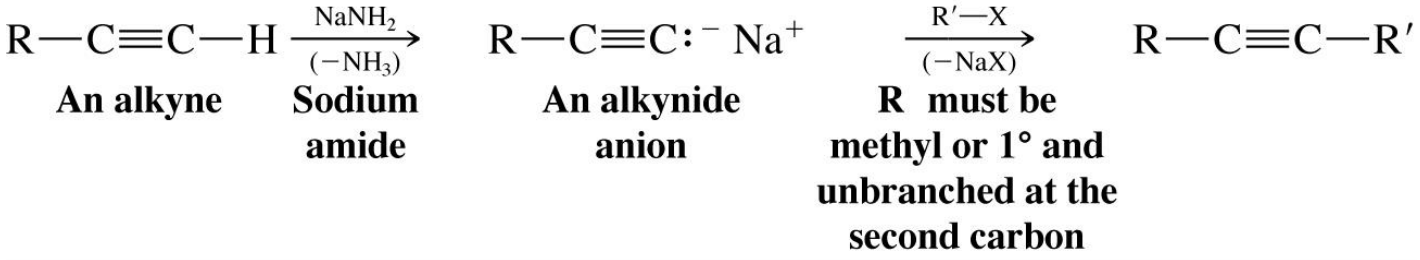
or*

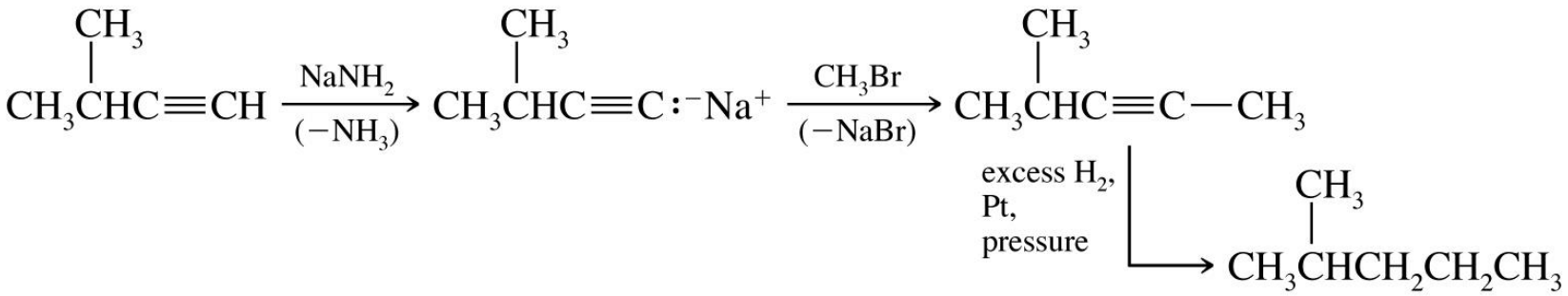
$$R{-}X \xrightarrow[(-ZnX_2)]{Zn,\ HX} R{-}H$$

$$2\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[Zn]{HBr} 2\ CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_3 + ZnBr_2$$

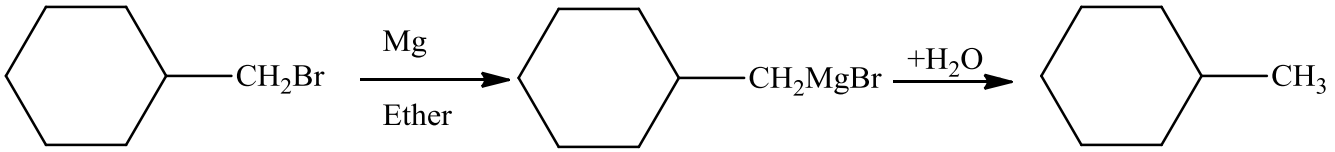
***sec*-Butyl bromide (2-bromobutane)** — **Butane**

- **Alkylation of Terminal Alkynes**
  - ➔ **Alkynes can be subsequently hydrogenated to alkanes**



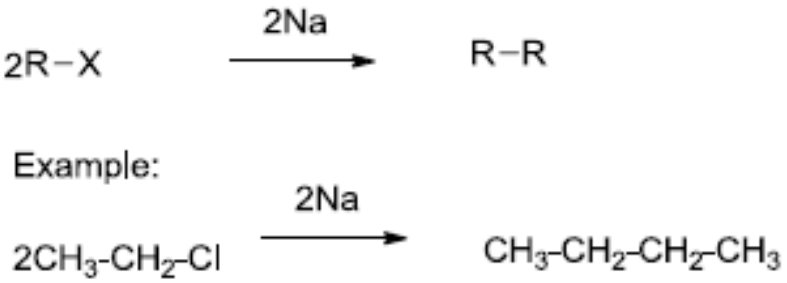


♦ Hydrolysis of Grignard reagent:



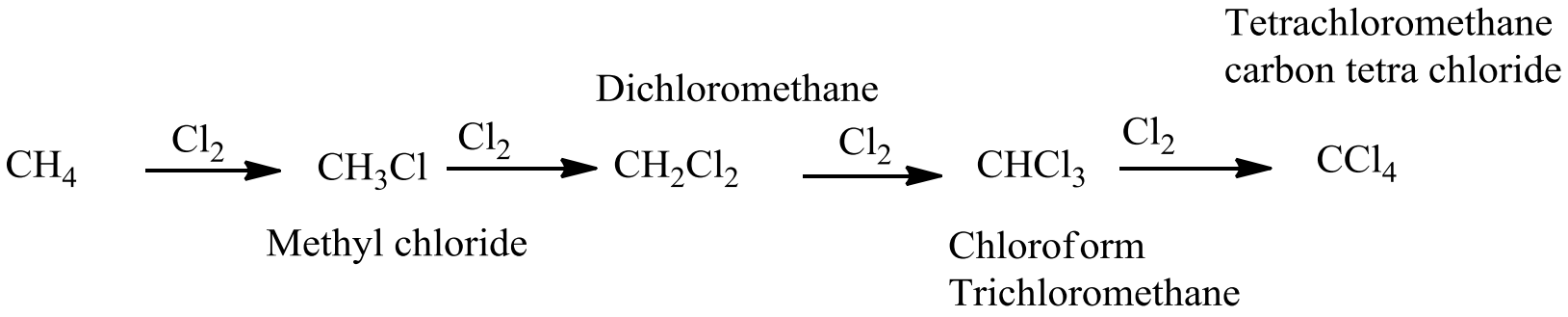
+ MgBr(OH)

♦ Wurtz (only symmetric alkane)



Reactions

Halogenations: (Chain reaction, Free Radical Substitution Reaction, happens in the presence of heat or sunlight (UV))



Subsititution reaction