2. ALKANES AND CYCLOALKANES

2.1 Nomenclature of Alkanes

Alkanes with increasing numbers of carbon atoms have names are based on the Latin word for the number of carbon atoms in the chain of each molecule.

Nomenclature of Straight Chain Alkanes:

n	C_nH_{2n+2}	n-Alkane	n	C_nH_{2n+2}	n-Alkane	n	C_nH_{2n+2}	n-Alkane
1	CH_4	methane	6	C_6H_{14}	hexane	11	$C_{11}H_{24}$	undecane
2	C_2H_6	ethane	7	C_7H_{16}	heptane	12	$C_{12}H_{26}$	dodecane
3	C_3H_8	propane	8	C_8H_{18}	octane	13	$C_{13}H_{28}$	tridecane
4	C_4H_{10}	butane	9	C_9H_{20}	nonane	14	$C_{14}H_{30}$	tetradecane
5	C_5H_{12}	pentane	10	$C_{10}H_{22}$	decane	15	$C_{15}H_{32}$	pentadecane

2.2 Physical Properties of Alkanes

(i) The first four alkanes are gases at room temperature. From pentane onwards, approximately the next twenty alkanes in the series are liquids and solids do not begin to appear until about $C_{17}H_{36}$. Alkanes with even longer chains are waxy solids room temperature.

(ii) There is no significant electronegativity difference between carbon and hydrogen. Thus, there is not any significant bond polarity. A totally symmetrical molecule like methane is completely non-polar. The boiling points and melting points of alkanes are lower than other organic compounds with the same molecular weight.

(iii) The boiling points and melting points increase as size of alkane increases (number of the carbon).

n	Formula	Name	b.p. (°C)	m.p. (°C)	Density (20°C) gml^{-1}
1	CH_4	methane	-161.7	-182.5	0.466 (at -164°C)
2	C_2H_6	ethane	-88.6	-183.3	0.572 (at -100°C)
3	C_3H_8	propane	-42.1	-187.7	0.585 (at -45°C)
4	C_4H_{10}	butane	-0.5	-138.3	0.5787
5	C_5H_{12}	pentane	36.1	-129.83	0.6262

(iv) Branched chain isomer has a lower boiling point than straight chain isomers.

	Pentane, C_5H_{12}	Isopentane	Neopentane
MW:	72g/mole	72	72
b.p:	36.1 °C	27.9 °C	9.5 °C

(v) Alkanes are soluble in nonpolar solvents such as benzene, hexane, and carbon tetrachloride. Both alkanes and cycloalkanes are insoluble in water, but able to mix with each other. Alkanes are also less dense than water.

2.3 Preparation of Alkanes

2.3.1 Hydrogenation of Alkenes and Alkynes

An alkene addition reaction is a process called hydrogenation. In a hydrogenation reaction, two hydrogen atoms are added to the double bond of an alkene, resulting in a saturated alkane.

$$\underset{\text{Alkene}}{RCH{=}CH_2} + H_2 \xrightarrow[P,\ \text{solvent}]{\text{catalyst}} \underset{\text{Alkane}}{RCH_2CH_3}$$

$$\underset{\text{Alkyne}}{RC{\equiv}CH} + H_2 \xrightarrow[P,\ \text{solvent}]{\text{catalyst}} \underset{\text{Alkane}}{RCH_2CH_3}$$

Catalyst: Pd, Pt, Ir, Raney Ni

2.3.2 Alkanes from Alkyl Halides

2.3.2.1 Reduction

Alkyl halides (except florides) on reduction with zinc and dilute HX give alkanes

$$\underset{\text{Haloalkane}}{R\text{-}X} + Zn + HX \longrightarrow \underset{\text{Alkane}}{R\text{-}H} + ZnX_2$$

X=Cl, Br, I

For this reduction reaction $LiAlH_4$, or H_2/ Catalyst (Pd, Pt, Ir, and Raney Ni) can be used as reduction reagent.

2.3.2.2 Wurtz Reaction

The Wurtz Reaction produces the simple dimer derived from two equivalents of alkyl halide. Using two different alkyl halides will lead to mixture of products

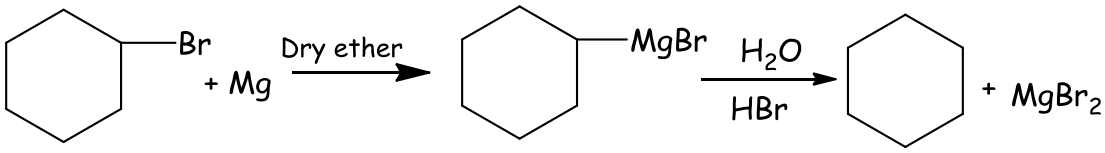
$$2R\text{-}X + 2Na\ (\text{or } 2K) \xrightarrow{\text{nonpolarsolvent},\ \Delta} R\text{-}R + 2\ NaCl\ (\text{ or } 2KCl)$$

$$2C_2H_5 - Cl + 2\ Na \rightarrow C_2H_5\text{-}C_2H_5 + 2NaCl$$

2.3.2.3 Hydrolysis of Grignard Reagent

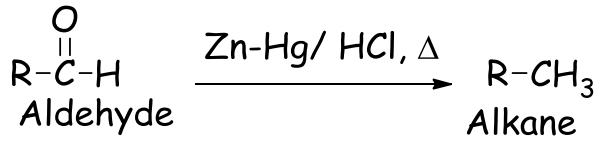
$$R^{\delta-}Mg^{\delta+}X \longrightarrow RMgX \xrightarrow[HCl]{H_2O} R - H + MgX_2$$

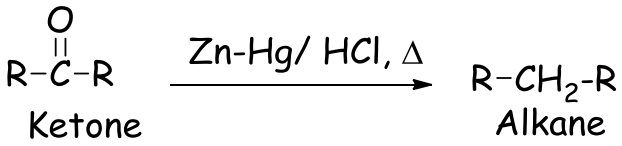
Grignard Reagent — Alkane



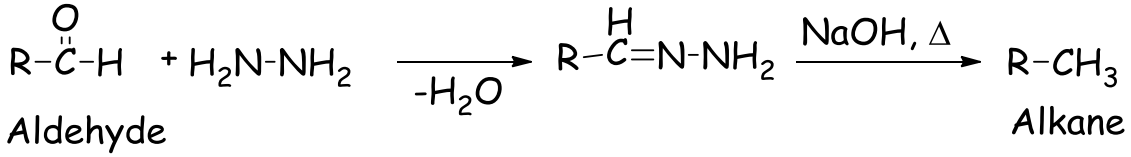
2.3.3 Reduction of Carbonyl Compounds

2.3.3.1 Clemmensen Reduction





2.3.3.2 Wolf- Kıschner Reduction



2.3.3.3 Alkanes from Carboxylic Acids

$$RCOONa + NaOH \longrightarrow R\text{-}H + Na_2CO_3$$

2.4 Reactions of Alkanes

Alkanes are inert compounds and are called paraffin's because they do not react as most chemicals. They are usually used as solvent or solution for extraction.

2.4.1 Radicalic substitution reactions (Halogenation):

Alkanes react with halogens in the presence of light /or (ultraviolet light - typically sunlight) and heat to replace H's with halogen's. Reaction takes place via radicalic mechanism.

$$R\text{-}H + X_2 \xrightarrow[\Delta]{h\nu} R\text{-}X + H\text{-}X$$

$$RCH_3 + Cl_2 \xrightarrow[\Delta]{h\nu} RCH_2Cl + HCl$$

X: Cl_2, Br_2

2.4.2 Combustion Reactions

$$C_nH_{2n+2} + (3n+1/2)\,O_2 \longrightarrow nCO_2 + (n+1)\,H_2O + \text{heat}$$

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat}$$

2.4.3 Cracking

Cracking has an important role in petroleum industry. Higher alkanes are converted into lower one by cracking.

$$CH_3\text{-}CH_2\text{-}CH_3 \longrightarrow \begin{cases} CH_3\text{-}CH{=}CH_2 + H_2 \\ CH{=}CH_2 + CH_4 \end{cases}$$

Presence of Cr_2O_3, V_2O_2, MoO_3 catalysis C-H bond cleavage

Presence of SiO_2, Al_2O_3, ZnO catalysis C-C bond cleavage

2.5 Cycloalkanes

Cycloalkanes are a cyclic structure with two or more carbon-containing compounds. General formula of cycloalkanes is C_nH2_n. The prefix cyclo- is added to the name of the alkane with the same number of carbons.

Cyclopropane cyclobutane cyclopentane cyclohexane