

BOOKS

- 1) Organic Chemistry Structure and Function, K. Peter C. Vollhardt, Neil Schore, 6th Edition
- 2) Organic Chemistry, T. W. Graham Solomons, Craig B. Fryhle
- 3) Organic Chemistry: A Short Course, H. Hart, L. E. Craine, D. J. Hart, C. M. Hadad,
- 4) Organic Chemistry: A Brief Course, R. C. Atkins, F.A. Carey

2. ALKANES AND CYCLOALKANES

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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:

<u>n</u>	<u>C_nH_{2n+2}</u>	<u>n-Alkane</u>	<u>n</u>	<u>C_nH_{2n+2}</u>	<u>n-Alkane</u>	<u>n</u>	<u>C_nH_{2n+2}</u>	<u>n-Alkane</u>
1	CH ₄	methane	6	C ₆ H ₁₄	hexane	11	C ₁₁ H ₂₄	undecane
2	C ₂ H ₆	ethane	7	C ₇ H ₁₆	heptane	12	C ₁₂ H ₂₆	dodecane
3	C ₃ H ₈	propane	8	C ₈ H ₁₈	octane	13	C ₁₃ H ₂₈	tridecane
4	C ₄ H ₁₀	butane	9	C ₉ H ₂₀	nonane	14	C ₁₄ H ₃₀	tetradecane
5	C ₅ H 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 C₁₇H₃₆. Alkanes with even longer chains are waxy solids room temperature.

(ii) Alkanes are typical covalent compounds. 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, meaning that the only attractions between one molecule and its neighbors will be Van der Waals dispersion forces. Forces between molecules are weak. 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). As mass increases, the London dispersion forces increases, then it causes the boiling point to increase. These forces will be very small for a molecule like methane but will increase as the molecules get bigger.

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 ₂ H ₆	ethane	-88.6	-183.3	0.572 (at -100°C)
3	C ₃ H ₈	propane	-42.1	-187.7	0.585 (at -45°C)
4	C ₄ H ₁₀	butane	-0.5	-138.3	0.5787
5	C ₅ H ₁₂	pentane	36.1	-129.83	0.6262

(iv) Branched chain isomer has a lower boiling point than a straight chain isomers. The branched alkanes have a low interaction surface, the London interaction decreases and hence boiling point decreases. Alkanes form homologous series.

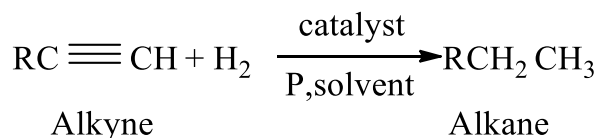
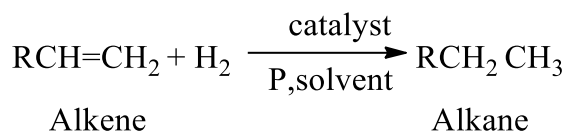
	<u>Pentane, C₅H₁₂</u>	<u>Isopentane</u>	<u>Neopentane</u>
MW:	72g/mole	72	72
b.p:	36.1 °C	27.9 °C	9.5 °C

(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 consisting of very weak dipole bonds cannot break the strong hydrogen bond between water molecules hence it is not miscible in water. Alkanes are also less dense than water.

2.3 Preparation of Alkanes

2.3.1 Hydrogenation of Alkenes and Alkynes

The double bond of an alkene consists of a sigma (σ) bond and a pi (π) bond. Because the carbon-carbon π bond is relatively weak, can be easily broken and hydrogens can be added to carbon. 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.

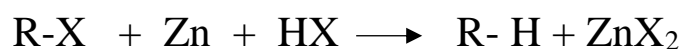


Catalyst: Pd, Pt, Ir, Raney Ni

2.3.2 Alkanes from Alkyl Halides

2.3.2.1 Reduction

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



Haloalkane

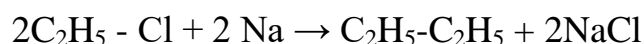
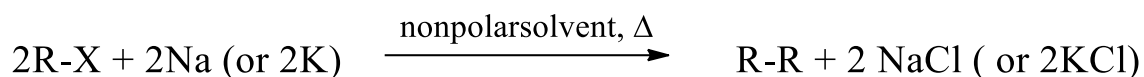
Alkane

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

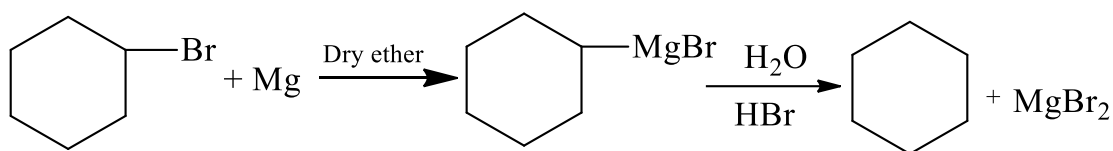


2.3.2.3 Hydrolysis of Grignard Reagent



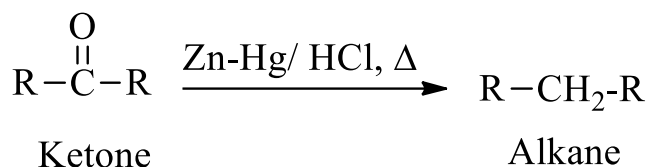
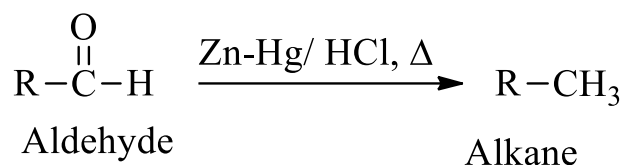
Grignard Reagent

Alkane

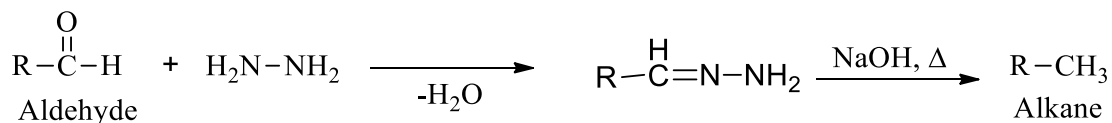


2.3.3 Reduction of Carbonyl Compounds

2.3.3.1 Clemmensen Reduction



2.3.3.2 Wolf- Kischner Reduction



2.3.3.3 Alkanes from Carboxylic Acids

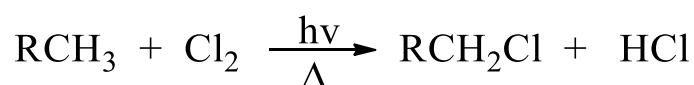
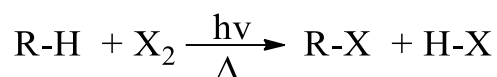


2.4 Reactions of Alkanes

Alkanes are inert compounds and are called paraffins because they do not react as most chemicals. This inertness is the source of the term paraffins (Latin para + affinis, with the meaning here of lacking affinity). They are usually used as solvent or solution for extraction.

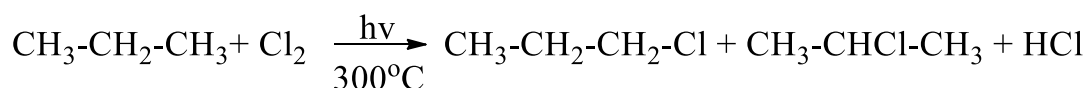
2.4.1 Radicalic substitution reactions (Halogenation):

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. Radical halogenation can yield a mixture of halogenated compounds because all hydrogen atoms in an alkane are capable of substitution.



X: Cl₂, Br₂

The chlorination and bromination of alkanes, product mixture is obtained depending on the position of hydrogen of the alkane (primary, secondary or tertiary hydrogens). Tertiary hydrogens are somewhat more reactive than secondary hydrogens which are more reactive than primary hydrogens



Propane

1-Chloropropane

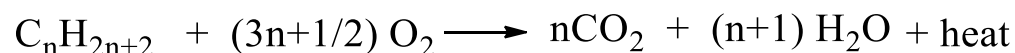
2-Chloropropane

(%50)

(%50)

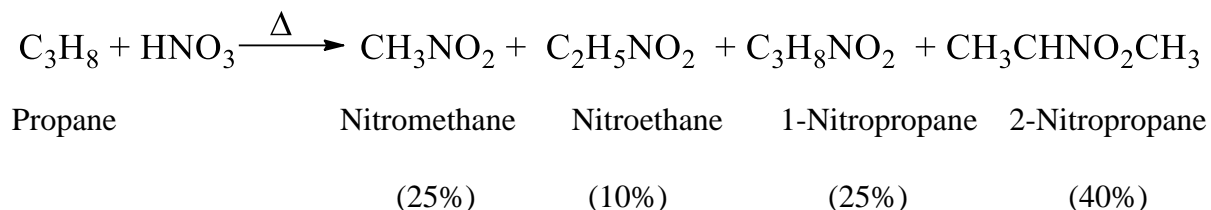
2.4.2 Combustion Reactions

Alkane's burn in the presence of oxygen to produce carbon dioxide and heat. In an environment of insufficient oxygen, air pollution can be caused due to release of excess carbon monoxide into the atmosphere



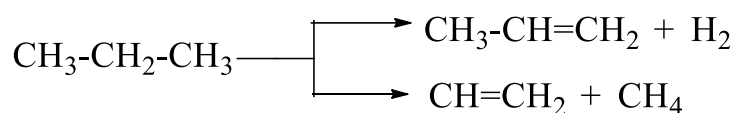
2.4.3 Nitration

Alkanes give these reactions at high temperatures with nitric acid vapors. In this type of reactions, the products are separated by distillation from each other.



2.4.4 Cracking

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



Presence of Cr_2O_3 , V_2O_5 , MoO_3 catalysis C-H bond cleavage

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

2.5 Cycloalkanes

2.5.1 Nomenclature of Cycloalkanes

Cycloalkanes are a cyclic structure with two or more carbon-containing compounds. General formula of cycloalkanes is C_nH_{2n} . The prefix cyclo- is added to the name of the alkane with the same number of carbons.



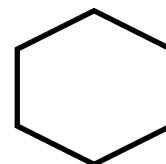
Cyclopropane



cyclobutane



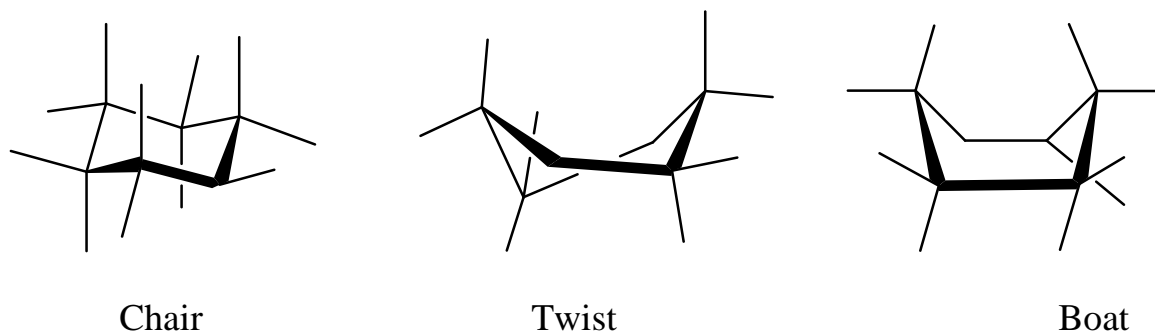
cyclopentane



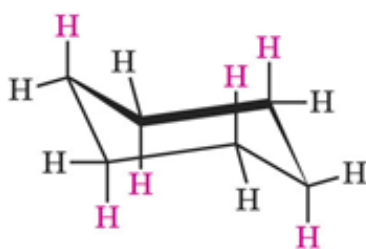
cyclohexane

2.5.2 Conformations of Cycloalkanes

Heats of combustion per CH_2 unit reveal cyclohexane has no ring strain and other cycloalkanes have some ring strain. The angle strain is caused by bond angles different from 109.5° and torsional strain is caused by eclipsing C-H bonds on adjacent carbons. Cyclopropane has both high angle and torsional strain. Cyclobutane has considerable angle strain and bends to relieve some torsional strain. Cyclopentane has little angle strain in the planar form but bends to relieve some torsional strain. There are three conformations of cyclohexane; chair, boat and twist. The chair conformation has no ring strain and all bond angles are 109.5° and all C-H bonds are perfectly staggered. The boat conformation is less stable because of the interactions and torsional strain along the bottom of the boat. The twist conformation is intermediate in stability between the boat and the chair conformation.



There are six axial hydrogen (shown in red) and six equatorial hydrogen (shown in black) in chair conformation of cyclohexane. Axial hydrogens are perpendicular to the average plane of the ring. Equatorial hydrogens lie around the perimeter of the ring. The C-C bonds and equatorial C-H bonds are all drawn in sets of parallel lines. The axial hydrogens are drawn straight up and down



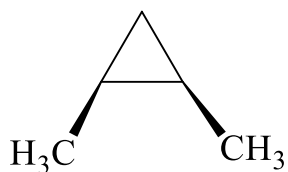
2.5.3 Substituted Cycloalkanes: Stereoisomers

Rotation about C-C bonds in cycloalkanes is limited by the ring structure. With two or more substituents, new type of isomerism occurs, which is stereoisomers. Stereoisomers are isomers with the same molecular formula and same connectivity of atoms but different arrangement of atoms in space. The terms “cis” and “trans” should be used to specify stereoisomeric ring structures.

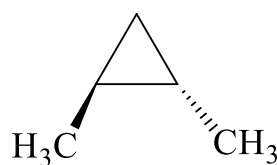
Cis: groups on same side of ring

Trans: groups on opposite side of ring

There are two different 1,2-dimethyl-cyclobutane isomers, one with the two methyl's on the same side (cis) of the ring and one with the methyl's on opposite sides (trans).



Cis-1,2-dimethylcyclopropane



Trans-1,2-dimethylcyclopropane

2.5.3.1 Monosubstituted Cycloalkanes

Methyl cyclohexane is more stable with the methyl equatorial. An axial methyl has an unfavorable 1,3-diaxial interaction with axial C-H bonds 2 carbons away. A 1,3-diaxial interaction is the equivalent of 2 gauche butane interactions.

2.5.3.1 Disubstitued Cycloalkanes

Disubstitued cycloalkanes can exist as pairs of cis-trans stereoisomers. *Trans*-1,4-dimethylcyclohexane prefers a *trans*-diequatorial conformation. *Cis*-1,4-dimethylcyclohexane exists in an axial-equatorial conformation. A very large *tert*-butyl group is required to be in the more stable equatorial position.