

CHM-134 ORGANIC CHEMISTRY

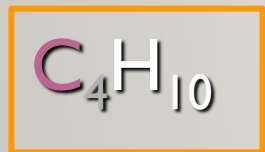
CHAPTER-2: ALKANES & CYCLOALKANES

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

Hydrocarbons **without**
functional groups

Straight chain: $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$

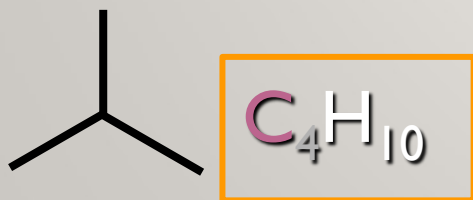
Line notation: 



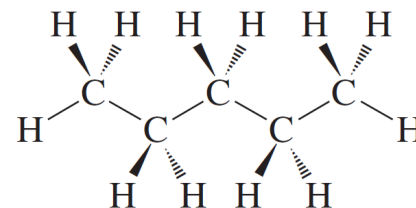
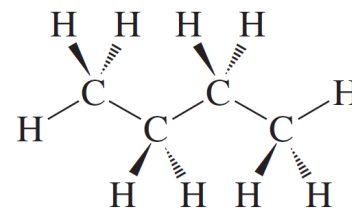
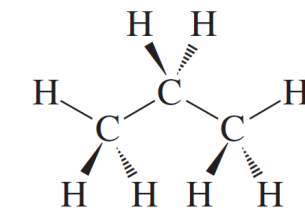
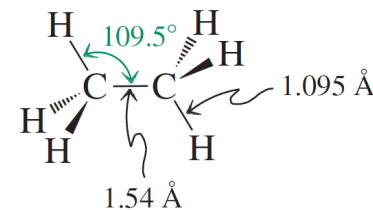
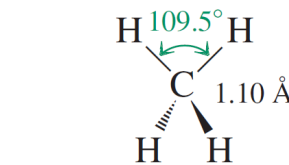
Butane

Branched: $\text{CH}_3 - \text{C}(\text{H})(\text{CH}_3) - \text{CH}_3$

Constitutional
isomers



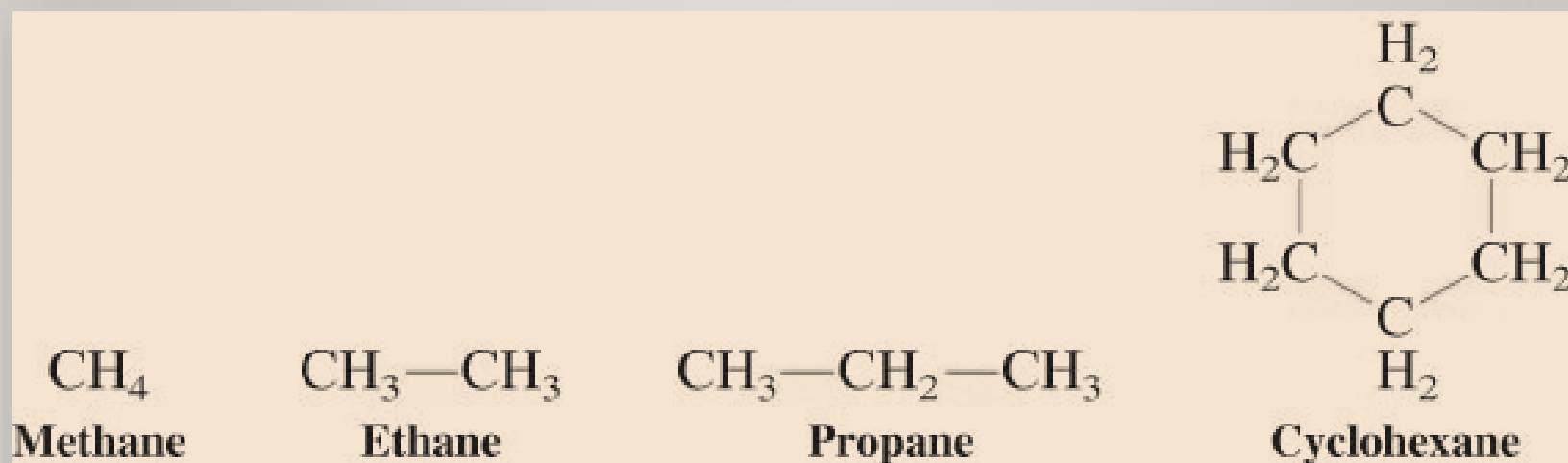
2-Methylpropane



2.1 FUNCTIONAL GROUPS

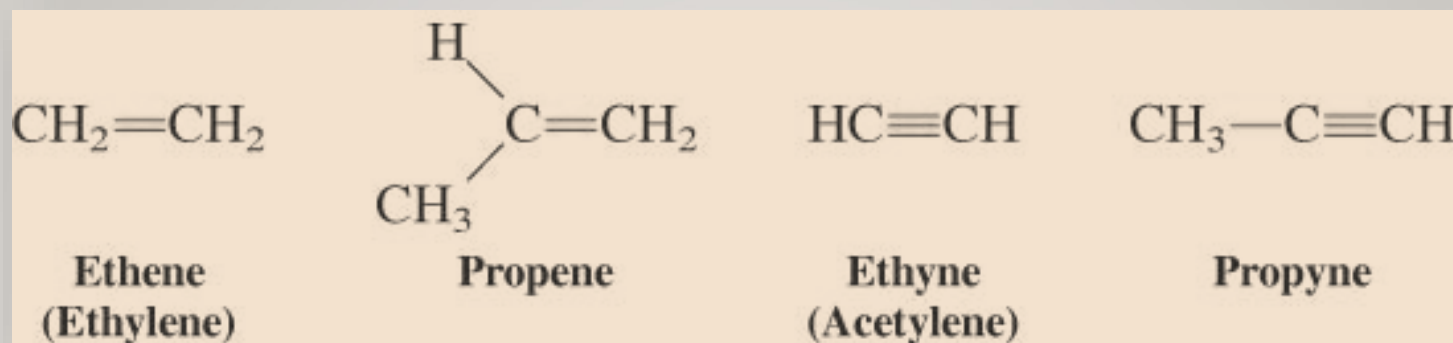
Functional groups are groups of atoms at sites of comparatively high chemical reactivity. They control the reactivity of the molecule as a whole.

- **Hydrocarbons are molecules that contain only hydrogen and carbon.**
- Alkanes are compounds of hydrogen and carbon which contain only single bonds.
- When the carbon atoms form a ring, the compounds are called cycloalkanes.

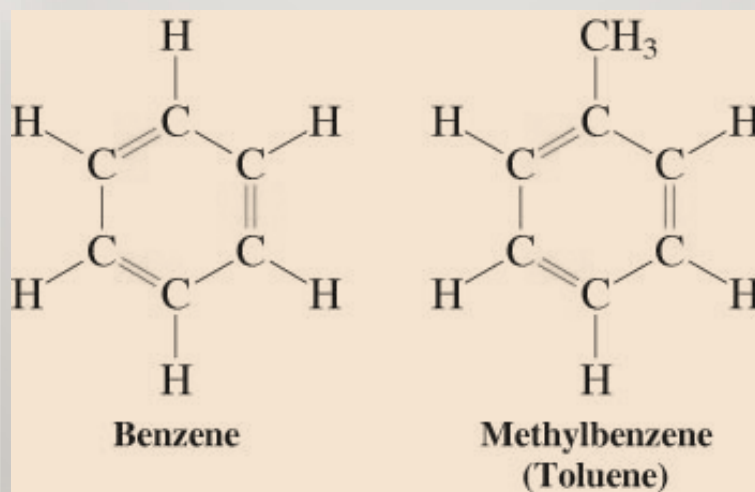


2.1 FUNCTIONAL GROUPS

Alkenes are hydrocarbons containing one or more C-C double bonds while alkynes contain one or more C-C triple bonds:

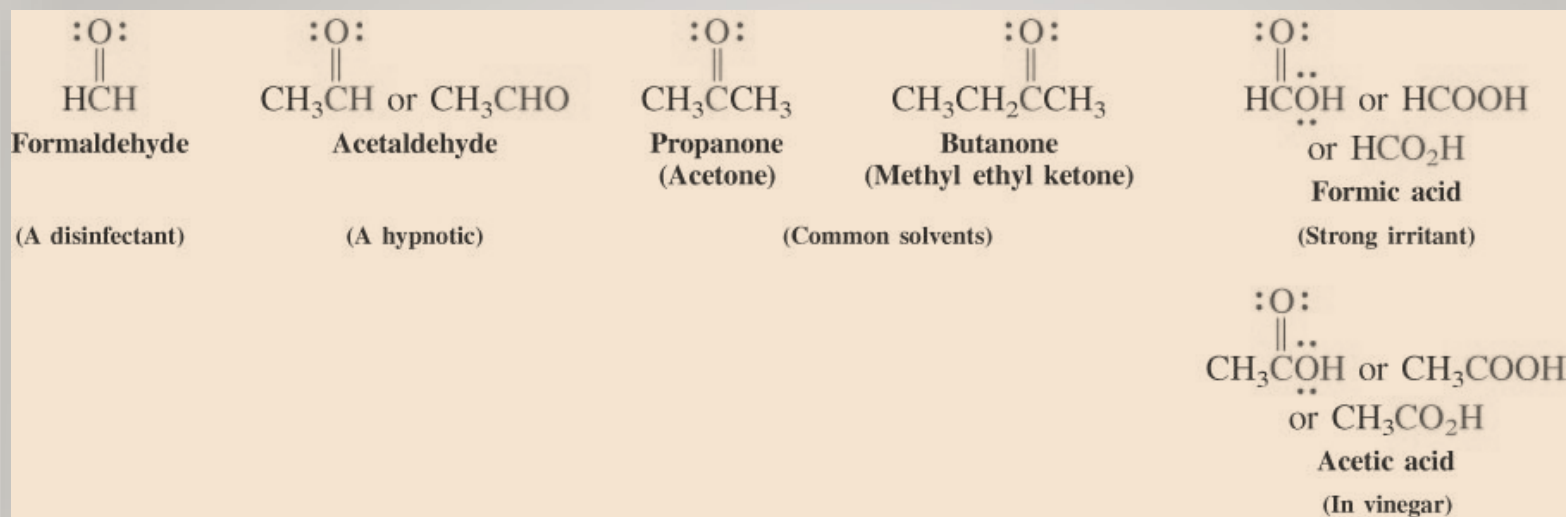


Benzene, C_6H_6 , and its derivatives are examples of the class of organic compounds called aromatic:

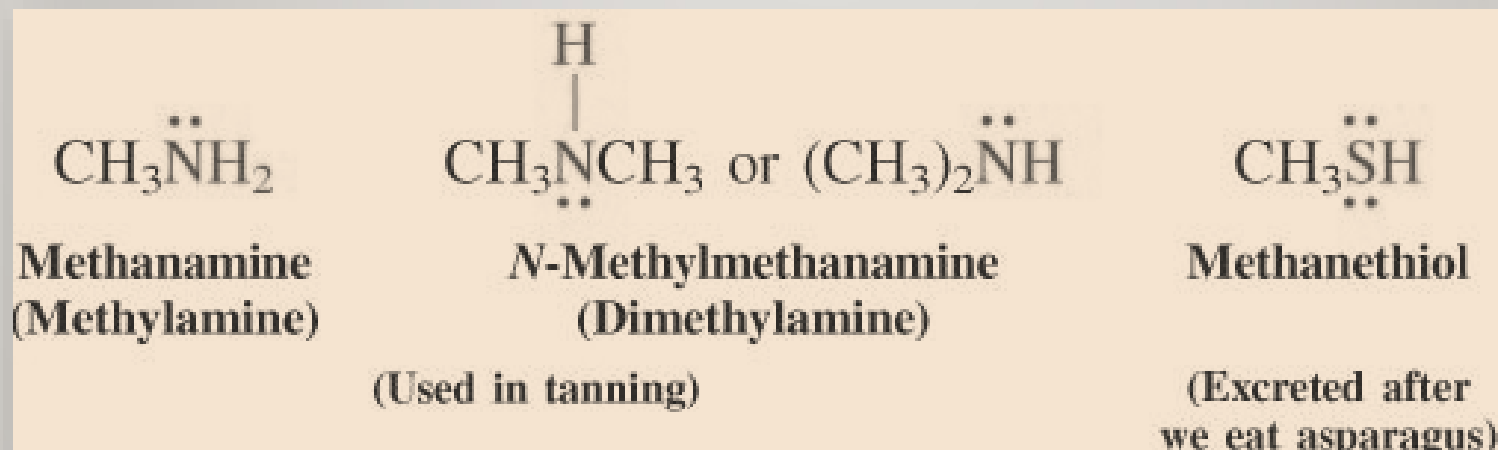


2.1 FUNCTIONAL GROUPS

The carbonyl functionality, C=O, is found in aldehydes, ketones, and carboxylic acids:



Alkyl nitrogen and sulfur compounds are named amines and thiols:



2.1 FUNCTIONAL GROUPS

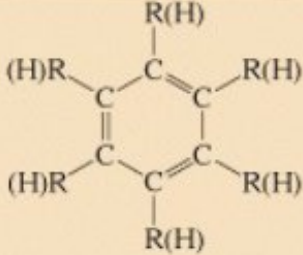
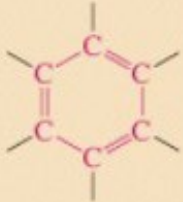
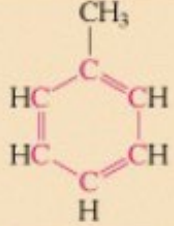
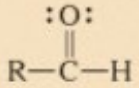
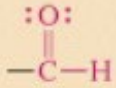
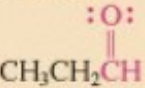
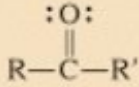
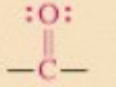
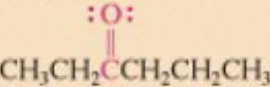
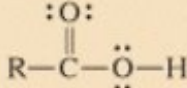
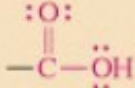
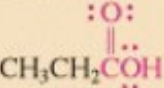
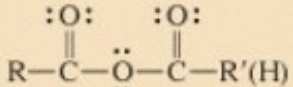
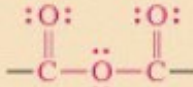

TABLE 2-3 Common Functional Groups

Compound class	General structure ^a	Functional group	Example
Alkanes	R—H	None	CH ₃ CH ₂ CH ₂ CH ₃ Butane
Haloalkanes	R— \ddot{X} : (X = F, Cl, Br, I)	— \ddot{X} :	CH ₃ CH ₂ — \ddot{Br} : Bromoethane
Alcohols	R— $\ddot{O}H$	— $\ddot{O}H$	$\begin{array}{c} H \\ \\ (CH_3)_2C-\ddot{O}H \end{array}$ 2-Propanol (Isopropyl alcohol)
Ethers	R— \ddot{O} —R'	— \ddot{O} —	CH ₃ CH ₂ — \ddot{O} —CH ₃ Methoxyethane (Ethyl methyl ether)
Thiols	R— $\ddot{S}H$	— $\ddot{S}H$	CH ₃ CH ₂ — $\ddot{S}H$ Ethanethiol
Alkenes	$\begin{array}{c} (H)R \\ \diagdown \\ C=C \\ \diagup \\ (H)R \end{array} \begin{array}{c} R(H) \\ \diagup \\ C=C \\ \diagdown \\ R(H) \end{array}$	$\diagdown C=C \diagup$	$\begin{array}{c} CH_3 \\ \diagdown \\ C=CH_2 \\ \diagup \\ CH_3 \end{array}$ 2-Methylpropene
Alkynes	(H)R—C≡C—R(H)	—C≡C—	CH ₃ C≡CCH ₃ 2-Butyne

^aThe letter R denotes an alkyl group (see text). Different alkyl groups can be distinguished by adding primes to the letter R: R', R'', and so forth.

2.1 FUNCTIONAL GROUPS

TABLE 2-3 Common Functional Groups (continued)

Compound class	General structure ^a	Functional group	Example
Aromatic compounds			 Methylbenzene (Toluene)
Aldehydes			 Propanal
Ketones			 3-Hexanone
Carboxylic acids			 Propanoic acid
Anhydrides			 Propanoic anhydride

^aThe letter R denotes an alkyl group (see text). Different alkyl groups can be distinguished by adding primes to the letter R: R', R'', and so forth.

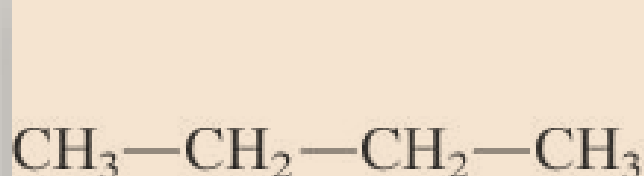
2.1 FUNCTIONAL GROUPS

TABLE 2-3 Common Functional Groups (continued)

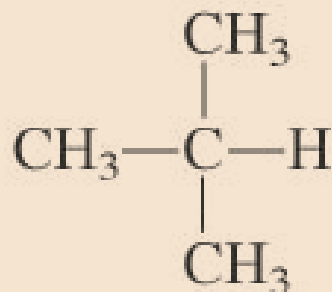
Compound class	General structure ^a	Functional group	Example
Esters	$\begin{array}{c} \text{:O:} \\ \parallel \\ (\text{H})\text{R}-\text{C}-\ddot{\text{O}}-\text{R}' \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\ddot{\text{O}}- \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{C}-\ddot{\text{O}}-\text{CH}_3 \\ \text{Methyl propanoate} \\ \text{(Methyl propionate)} \end{array}$
Amides	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{R}-\text{C}-\ddot{\text{N}}-\text{R}'(\text{H}) \\ \\ \text{R}''(\text{H}) \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ -\text{C}-\ddot{\text{N}}- \\ \end{array}$	$\begin{array}{c} \text{:O:} \\ \parallel \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{C}-\ddot{\text{N}}\text{H}_2 \\ \text{Butanamide} \end{array}$
Nitriles	$\text{R}-\text{C}\equiv\text{N:}$	$-\text{C}\equiv\text{N:}$	$\text{CH}_3\text{C}\equiv\text{N:}$ Ethanenitrile (Acetonitrile)
Amines	$\begin{array}{c} \ddot{\text{N}} \\ \\ \text{R}-\text{N}-\text{R}'(\text{H}) \\ \\ \text{R}''(\text{H}) \end{array}$	$-\ddot{\text{N}}\begin{array}{l} \diagup \\ \diagdown \end{array}$	$(\text{CH}_3)_3\text{N:}$ <i>N,N</i> -Dimethylmethanamine (Trimethylamine)

2.2 ALKANES

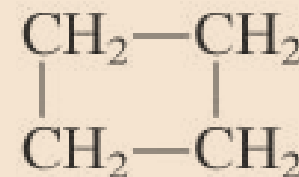
Alkanes can be classified into three general classes: **straight-chain alkanes**, **branched alkanes**, and **cycloalkanes**:



Butane, C_4H_{10}



2-Methylpropane, C_4H_{10}
(Isobutane)



Cyclobutane, C_4H_8

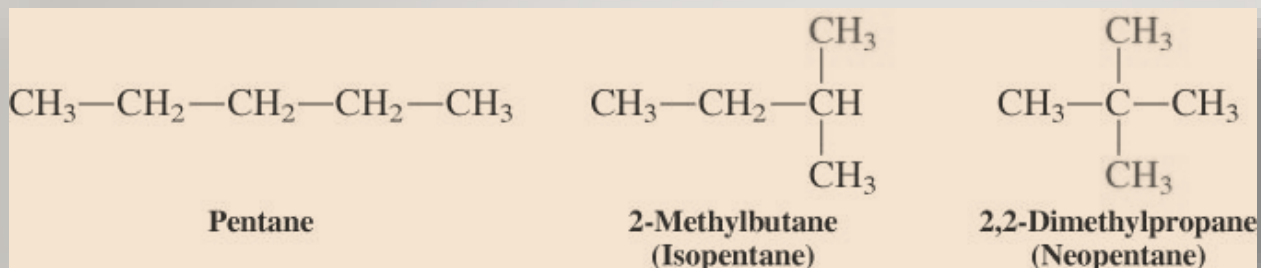
- ❑ Straight-chain alkanes form a homologous series.
- ❑ The general formula of a straight chain alkane is $\text{C}_n\text{H}_{2n+2}$.
- ❑ Each member of the series differs from the previous one by the addition of a $-\text{CH}_2-$, or methylene, group.
- ❑ Molecules related in this manner are called homologs of each other and the series is called a homologous series.

2.2 ALKANES

Branched alkanes are constitutional isomers of straight-chain alkanes.

Branched chain alkanes have the same molecular formula as straight chain alkanes, C_nH_{2n+2} , but differ in connectivity. A branched and straight chain alkane are constitutional isomers of each other.

There are three isomeric pentanes:



The number of isomeric alkanes increases dramatically with the number of carbon atoms:

TABLE 2-4	
Number of Possible Isomeric Alkanes, C_nH_{2n+2}	
n	Isomers
1	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
15	4,347
20	366,319

2.2 ALKANES

Many common or trivial names are still used widely used to name certain alkanes.

Systematic IUPAC names are more precise.

The first 20 straight chain alkanes are:

TABLE 2-5

Names and Physical Properties of Straight-Chain Alkanes, C_nH_{2n+2}

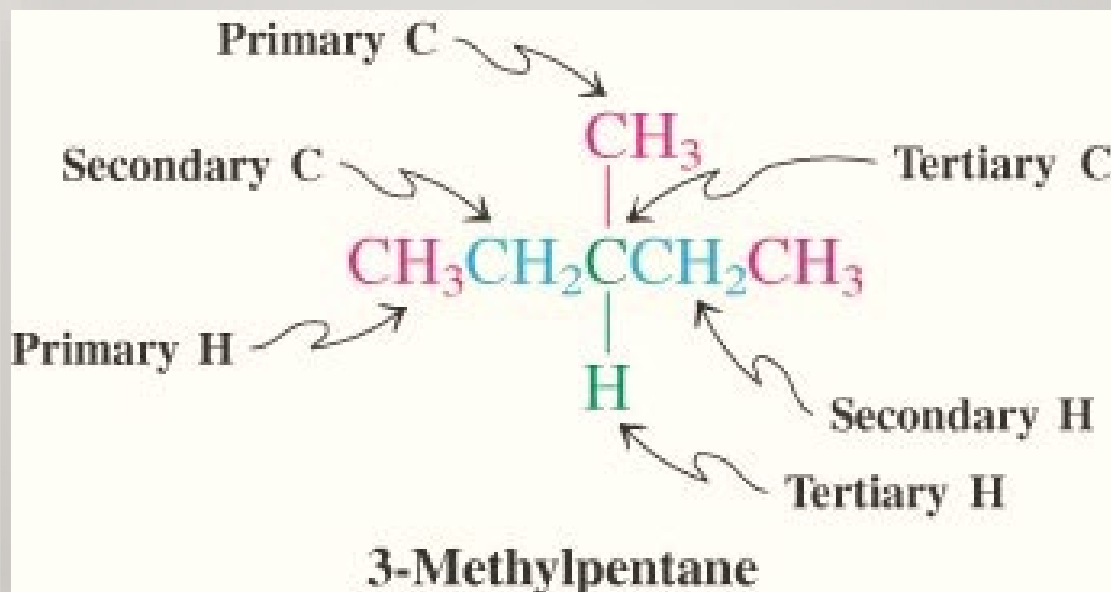
<i>n</i>	Name	Formula	Boiling point (°C)	Melting point (°C)	Density at 20°C (g ml ⁻¹)
1	Methane	CH ₄	-161.7	-182.5	0.466 (at -164°C)
2	Ethane	CH ₃ CH ₃	-88.6	-183.3	0.572 (at -100°C)
3	Propane	CH ₃ CH ₂ CH ₃	-42.1	-187.7	0.5853 (at -45°C)
4	Butane	CH ₃ CH ₂ CH ₂ CH ₃	-0.5	-138.3	0.5787
5	Pentane	CH ₃ (CH ₂) ₃ CH ₃	36.1	-129.8	0.6262
6	Hexane	CH ₃ (CH ₂) ₄ CH ₃	68.7	-95.3	0.6603
7	Heptane	CH ₃ (CH ₂) ₅ CH ₃	98.4	-90.6	0.6837
8	Octane	CH ₃ (CH ₂) ₆ CH ₃	125.7	-56.8	0.7026
9	Nonane	CH ₃ (CH ₂) ₇ CH ₃	150.8	-53.5	0.7177
10	Decane	CH ₃ (CH ₂) ₈ CH ₃	174.0	-29.7	0.7299

2.2 ALKANES

An alkyl group is formed by removing a hydrogen from an alkane. It is named by removing the -ane suffix and replacing it by -yl.

CH_3 - methyl; CH_3CH_2 - ethyl; $\text{CH}_3\text{CH}_2\text{CH}_2$ - propyl

Additional prefixes are also used: sec- (or s-) for secondary, and tert- (or t-) for tertiary. A secondary carbon is directly attached to two other carbons. A tertiary carbon is directly attached to three other carbons.



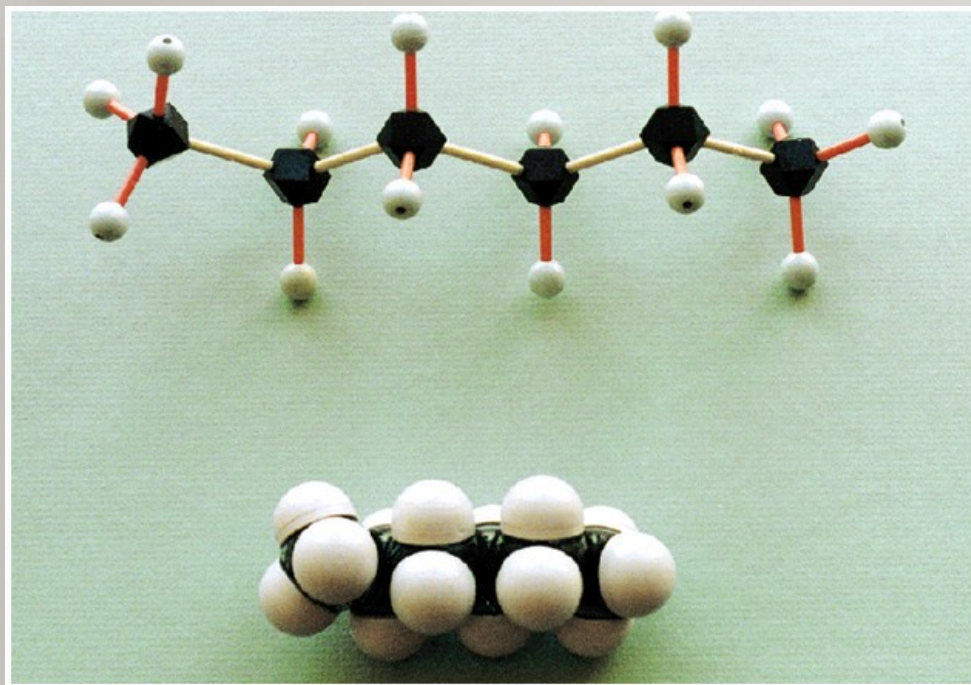
2.2 ALKANES

Some common branched alkyl groups are:

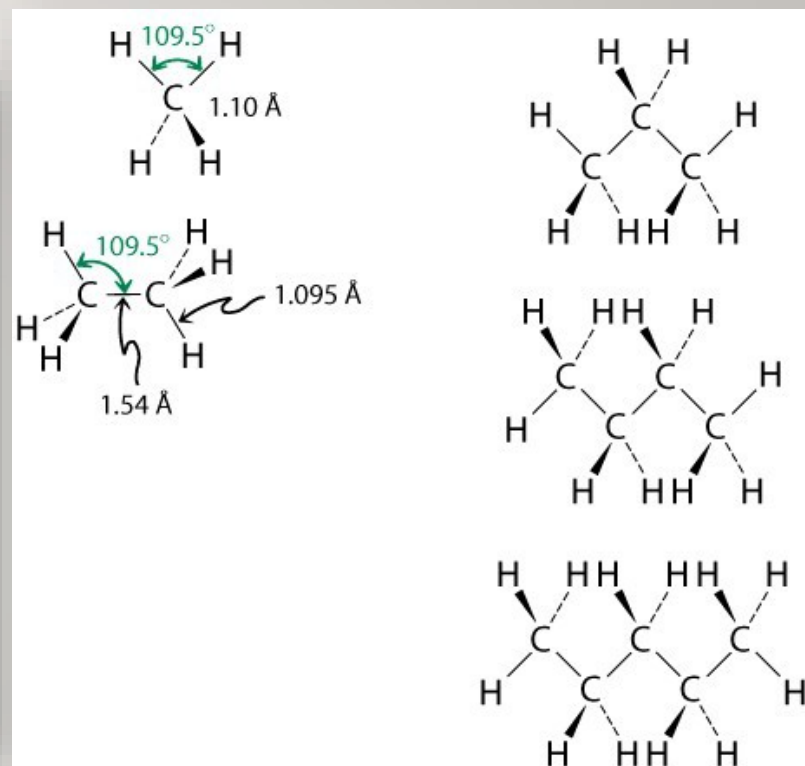
Structure	Common name	Example of common name in use	Systematic name	Type of group
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}- \\ \\ \text{H} \end{array}$	Isopropyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Cl} \text{ (Isopropyl chloride)} \\ \\ \text{H} \end{array}$	1-Methylethyl	Secondary
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2- \\ \\ \text{H} \end{array}$	Isobutyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_3 \text{ (Isobutane)} \\ \\ \text{H} \end{array}$	2-Methylpropyl	Primary
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}- \\ \\ \text{H} \end{array}$	<i>sec</i> -Butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{NH}_2 \text{ (} \textit{sec}\text{-Butyl amine)} \\ \\ \text{H} \end{array}$	1-Methylpropyl	Secondary
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}- \\ \\ \text{CH}_3 \end{array}$	<i>tert</i> -Butyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Br} \text{ (} \textit{tert}\text{-Butyl bromide)} \\ \\ \text{CH}_3 \end{array}$	1,1-Dimethylethyl	Tertiary
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	Neopentyl	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{OH} \text{ (Neopentyl alcohol)} \\ \\ \text{CH}_3 \end{array}$	2,2-Dimethylpropyl	Primary

2.2 ALKANES

Alkanes exhibit regular molecular structures and properties.

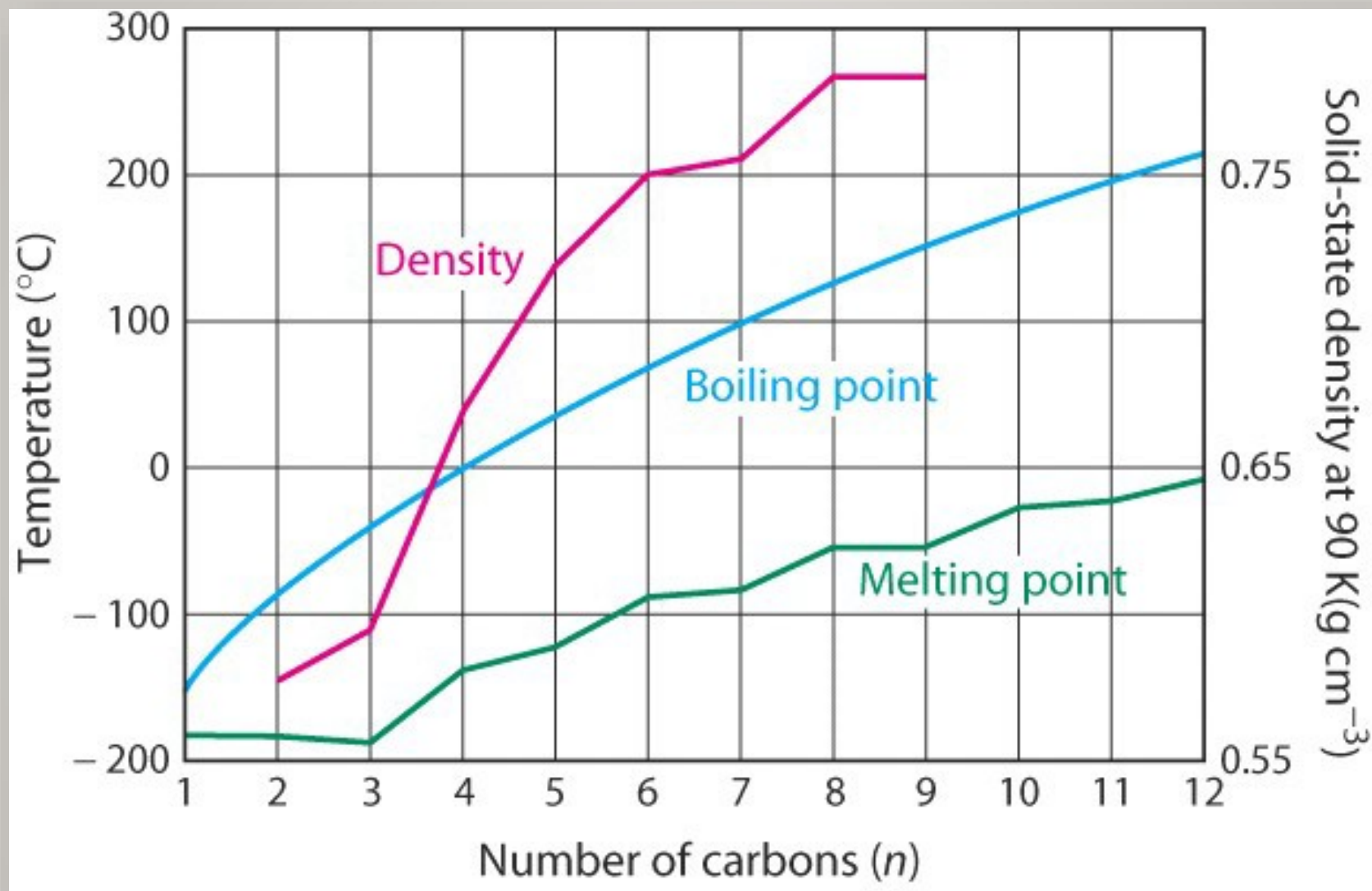


The carbon atoms are tetrahedral (bond angles close to 109°), C-C bond lengths all $\sim 1.54 \text{ \AA}$, and C-H bond lengths all $\sim 1.10 \text{ \AA}$.



2.2 ALKANES

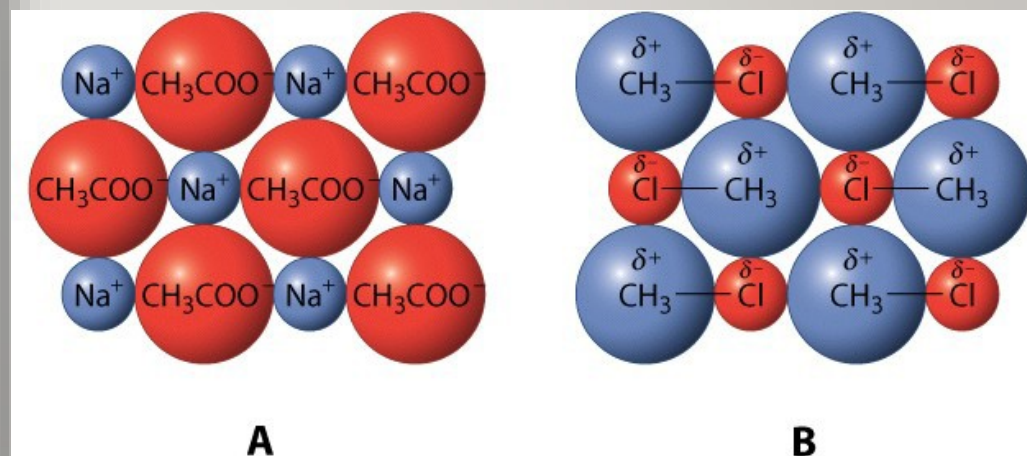
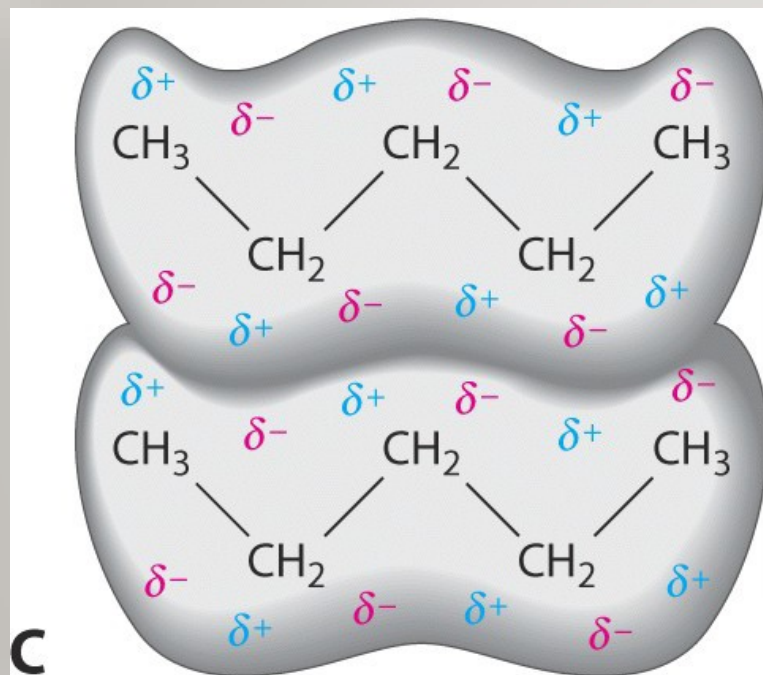
The physical constants of alkanes follow predictable trends:



2.2 ALKANES

Attractive forces between molecules govern the physical properties of alkanes.

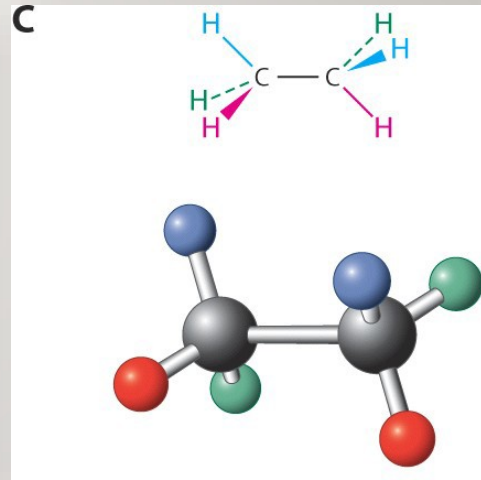
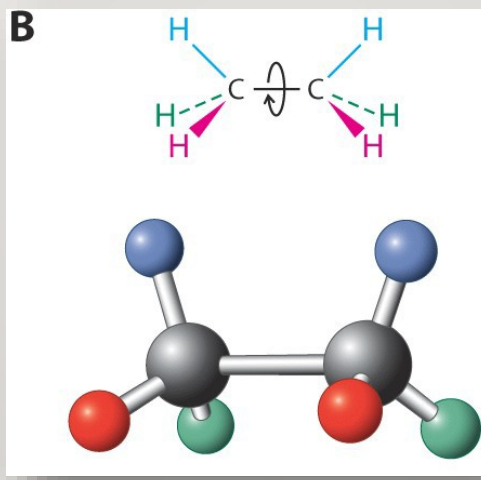
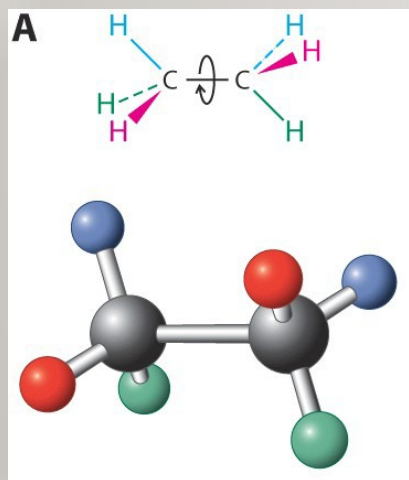
- The physical forces between alkane molecules are due to London forces. These forces arise from the correlation of electron motion on neighboring molecules.
- London forces are very weak and fall off with the 6th power of the distance between molecules (Coulomb forces fall off with the 2nd power).



2.2 ALKANES

Rotation interconverts the conformations of ethane

- ❑ The barrier to rotation of the two methyl groups in ethane is approximately 2.9 kcal/mol. Since this amount of energy is readily available at room temperature from molecular collisions, the methyl groups are said to have free rotation.
- ❑ The rotation motions within ethane can be represented by the dashed/wedged notation:

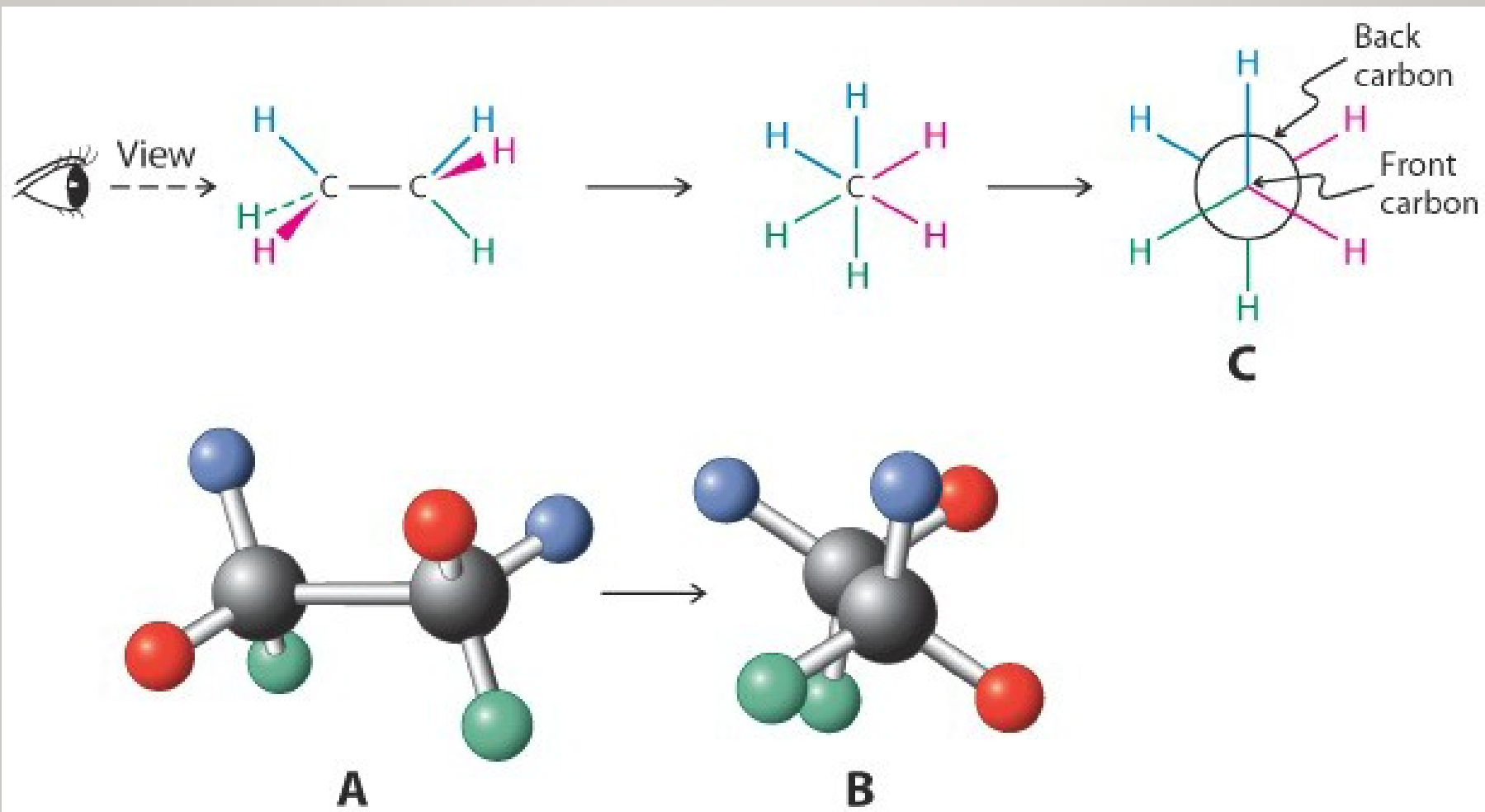


During the rotation, the conformation moves from the staggered to the eclipsed, and to a second staggered conformation.

2.2 ALKANES

Newman projections depict the conformations of ethane.

The Newman projection is an alternative to using the dashed/ wedged notation:

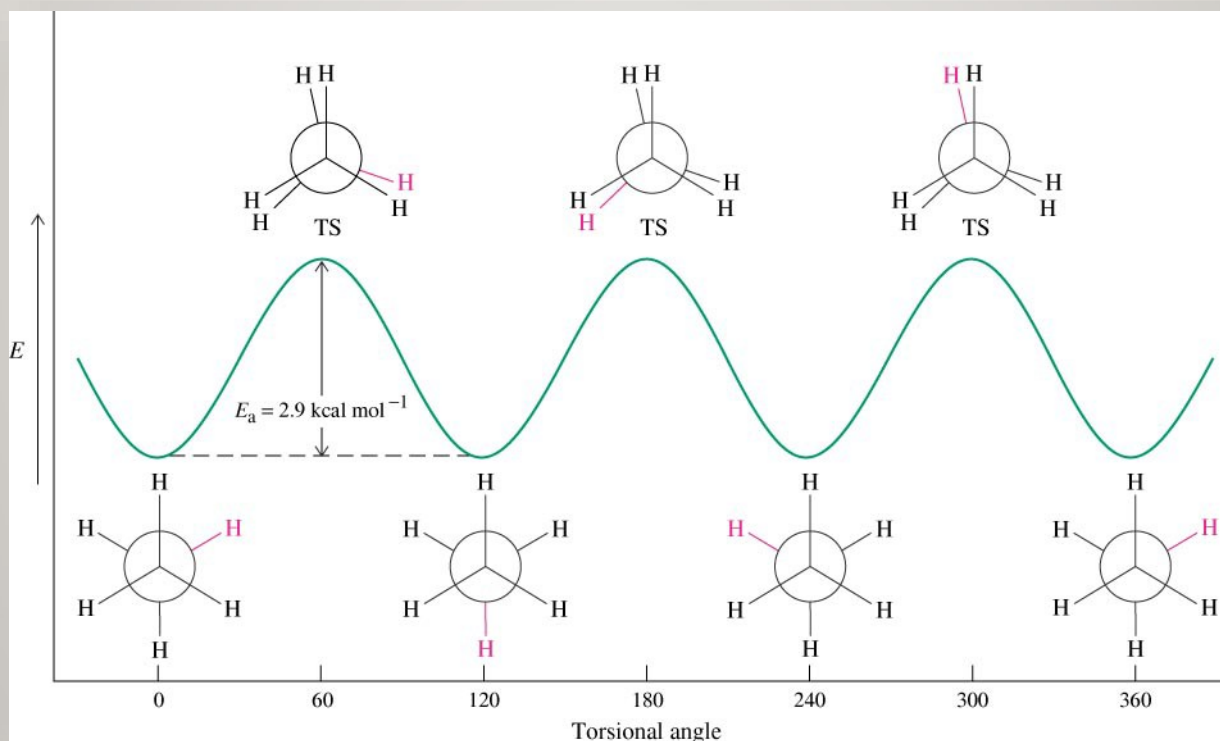


2.2 ALKANES

The rotamers of ethane have different potential energies.

The point of lowest potential during the C-C bond rotation in ethane is at the staggered conformation, the highest potential energy is at the eclipsed conformation (about 2.9 kcal/mole higher).

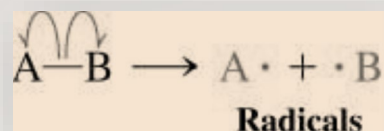
The lifetime of the eclipsed conformation is extremely short, and this conformation represents a transition state connecting two staggered conformations.



2.2 ALKANES

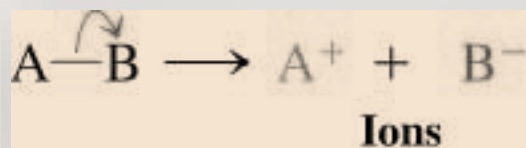
Radicals are formed by homolytic cleavage.

- When a bond breaks leaving the bonding electrons equally divided between the atoms, the process is called **homolytic cleavage or homolysis**:



- Species containing more than one atom and an unpaired electron are called radicals.
- Free atoms and radicals exist as intermediates in small concentrations during the course of many reactions but cannot usually be isolated.

Heterolytic cleavage results in the formation of ions, rather than radicals:



Homolytic Cleavage:

Nonpolar solvents

Gas phase

Heterolytic Cleavage:

Polar solvents (stabilize ions)

Electronegativities of atoms support ion formation

2.2 ALKANES

TABLE 3-1

Bond-Dissociation Energies of Various A-B Bonds
(DH° in kcal mol⁻¹)

A in A-B	B in A-B						
	-H	-F	-Cl	-Br	-I	-OH	-NH ₂
H—	104	136	103	87	71	119	108
CH ₃ —	105	110	85	70	57	93	84
CH ₃ CH ₂ —	101	111	84	70	56	94	85
CH ₃ CH ₂ CH ₂ —	101	110	85	70	56	92	84
(CH ₃) ₂ CH—	98.5	111	84	71	56	96	86
(CH ₃) ₃ C—	96.5	110	85	71	55	96	85

Note: These numbers are being revised continually because of improved methods for their measurement. Some of the values given here may be in (small) error.

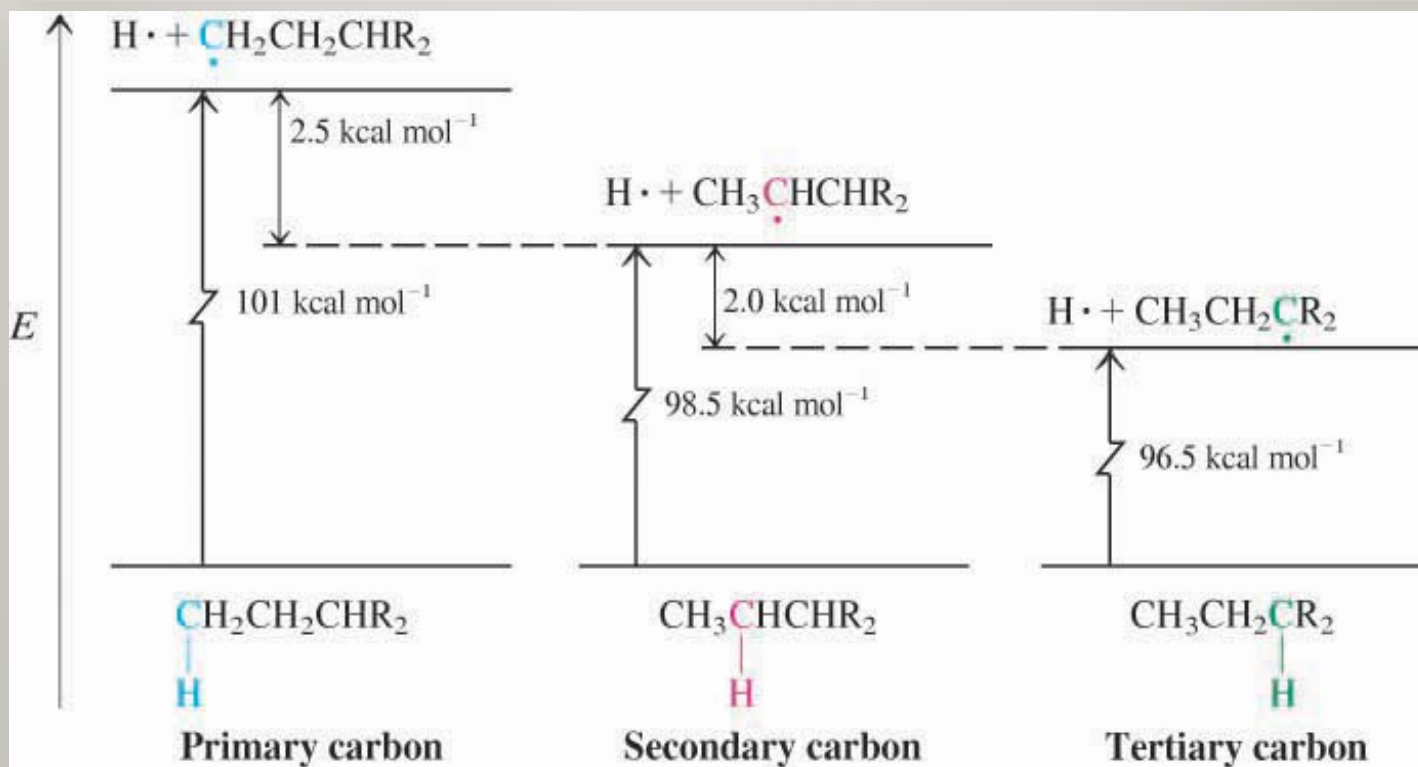
2.2 ALKANES

The stability of radicals determines the C-H bond strengths.

- ❖ The bond dissociation energies in alkanes generally decreases with the progression:
Methane > Primary > Secondary > Tertiary

Radical stability increases (and thus the energy required to create them decreases) in the progression:

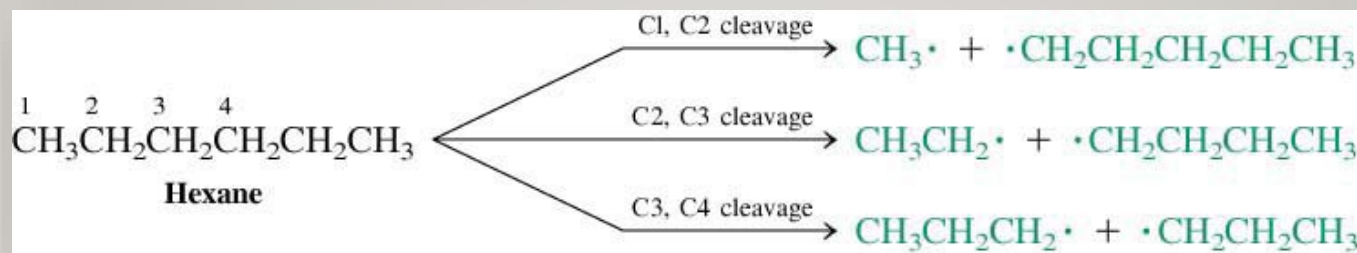
$\text{CH}_3 < \text{primary} < \text{secondary} < \text{tertiary}$



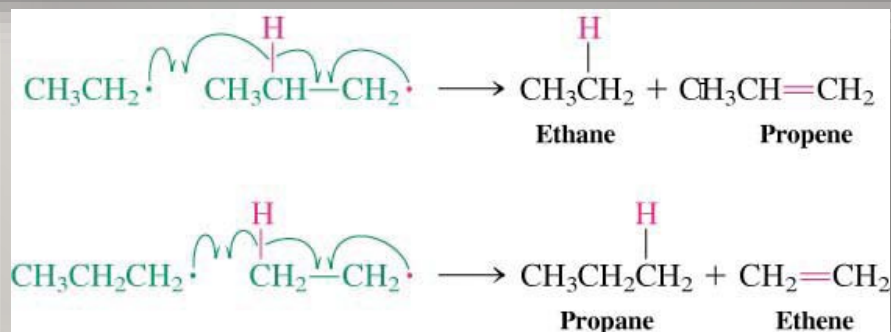
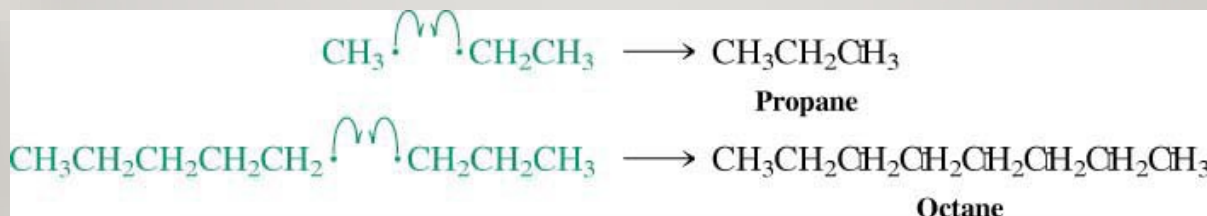
2.2 ALKANES

High temperatures cause bond homolysis.

Both C-H and C-C bonds are ruptured at high temperature in a process called pyrolysis.



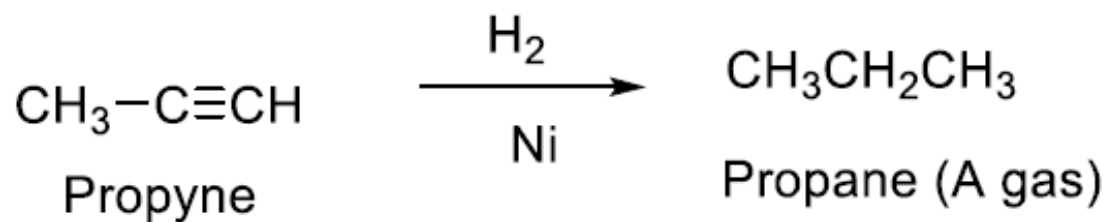
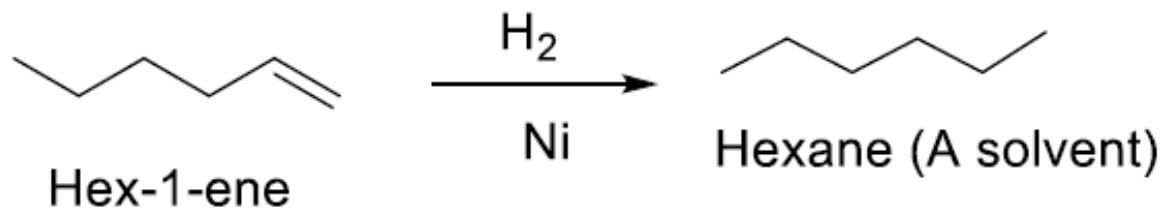
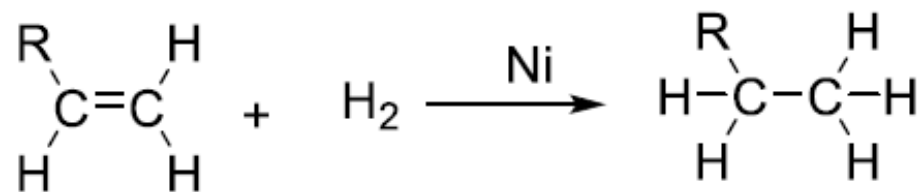
The resulting radicals can combine to form higher or lower molecular weight compounds, or form alkenes by further hydrogen extraction:



2.2 ALKANES

General Methods of Preparation of Alkanes

I. Catalytic hydrogenation of alkenes or alkynes

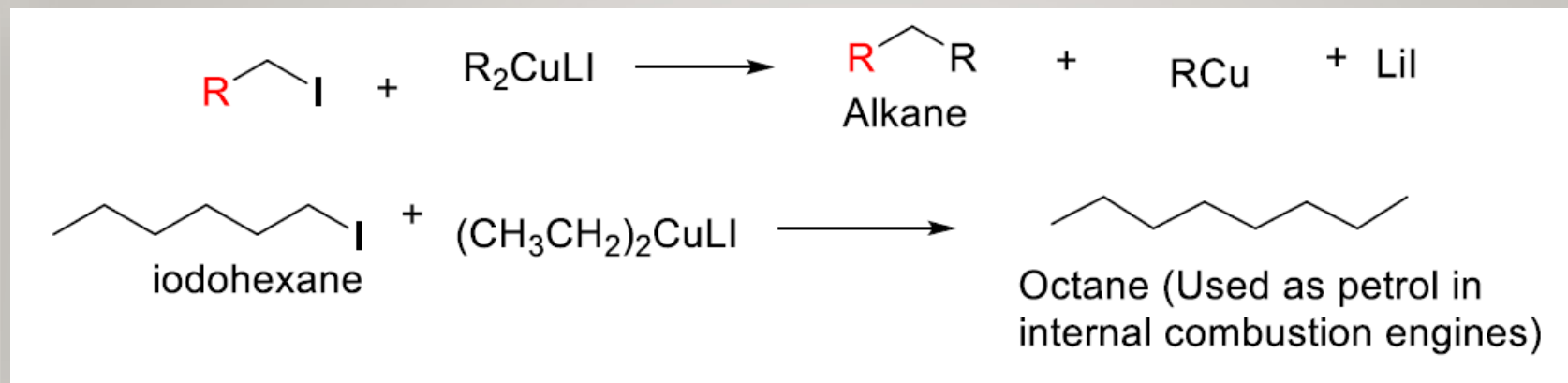


Catalytic hydrogenation is the common method for converting unsaturated oils to saturated fats in a process commonly referred to as “hardening of oils”.

2.2 ALKANES

General Methods of Preparation of Alkanes

2. Organocuprates (Gilman reagents) couple with alkyl halides to provide alkanes



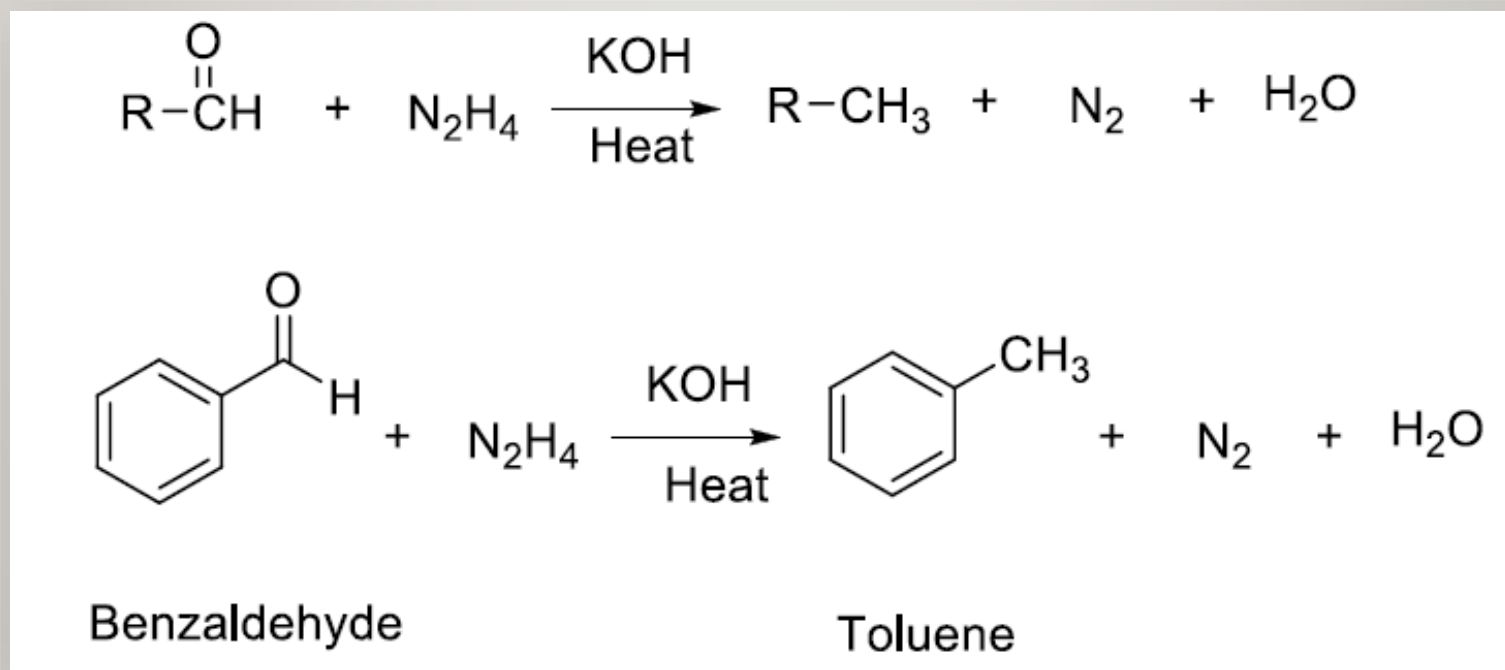
- ❖ The reaction of organocuprates with alkyl halides is a substitution reaction made possible by the polarization of the C-I as a result of the differences in electronegativities between carbon and iodine.
- ❖ Note that the C-Cu bond is less polarized and therefore more covalent compared with the C-Li or C-Mg bonds.

2.2 ALKANES

General Methods of Preparation of Alkanes

4. Reduction (deoxygenation) of aldehydes and ketones also provides access to hydrocarbons.

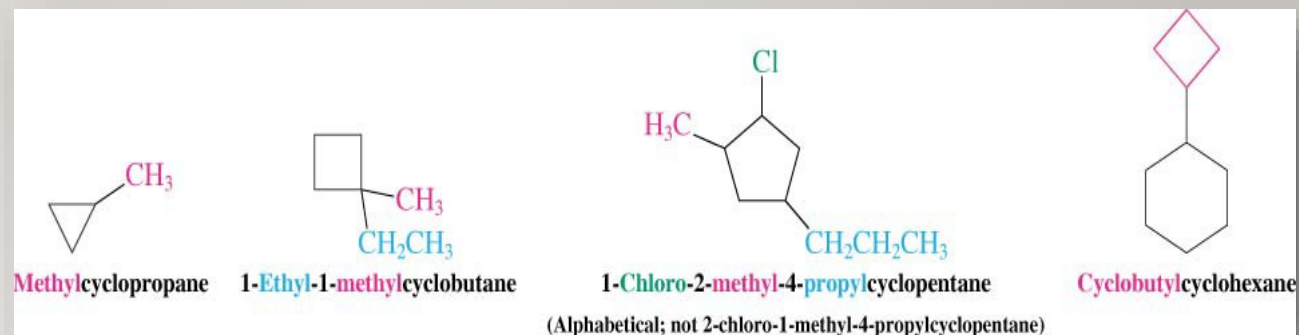
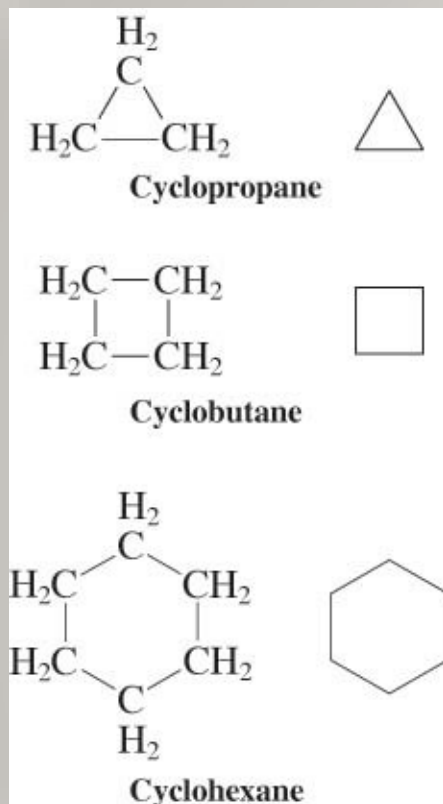
- ❑ One of the most common methods for deoxygenation of aldehydes and ketones is the Wolff-Kishner reduction.
- ❑ It involves heating an aldehyde or ketone with hydrazine in the presence of a base (KOH).



<https://www.askiitians.com/iit-jee-chemistry/organic-chemistry/general-methods-of-preparation-of-alkanes.aspx>

2.3 CYCLOALKANES

The names of the cycloalkanes follow IUPAC rules.



- ❑ Numbering a cycloalkane ring is necessary only when there is more than one substituent. In non-substituted cycloalkanes, the attached carbon is numbered number 1.
- ❑ Use the lowest possible numbering sequence for polysubstituted cycloalkanes. If two identical numbering sequences are possible, use alphabetical precedence.
- ❑ Substituted cycloalkanes are sometimes named as cycloalkyl derivatives. The smaller unit is generally treated as a substituent to the larger unit.

To name a cycloalkane, prefix the alkane name with “cyclo”.

2.3 CYCLOALKANES

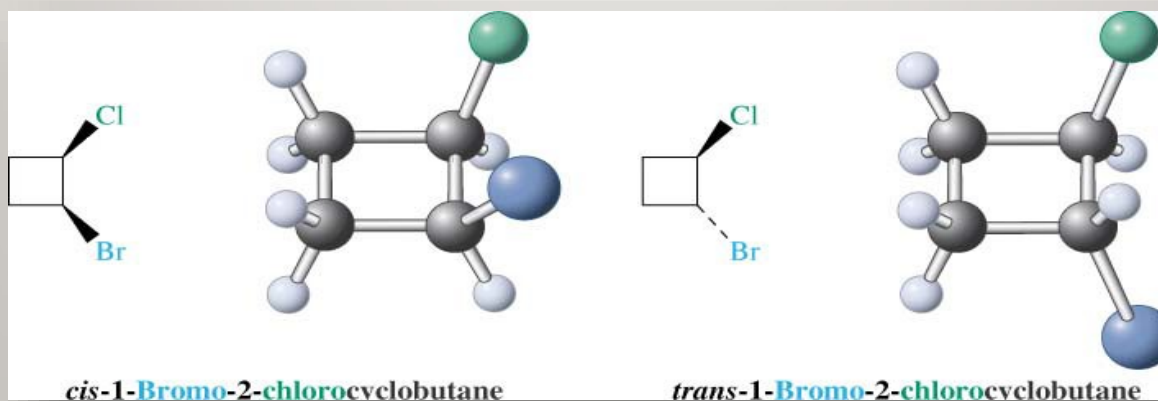
Disubstituted cycloalkanes possess stereoisomers.

Disubstituted cycloalkanes having substituents on different carbons possess cis (same side) / trans (opposite side) isomers.



Cis/trans isomers are examples of stereoisomers. These are non- superimposable molecules having the same molecular formula and connectivity.

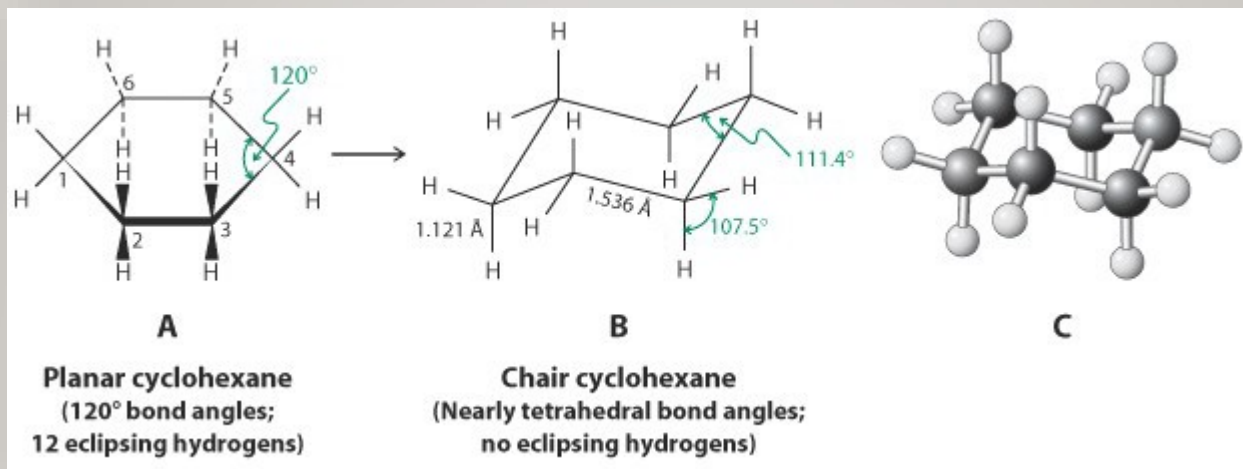
Conformers are also stereoisomers but can be interconverted by rotations about C-C bonds.



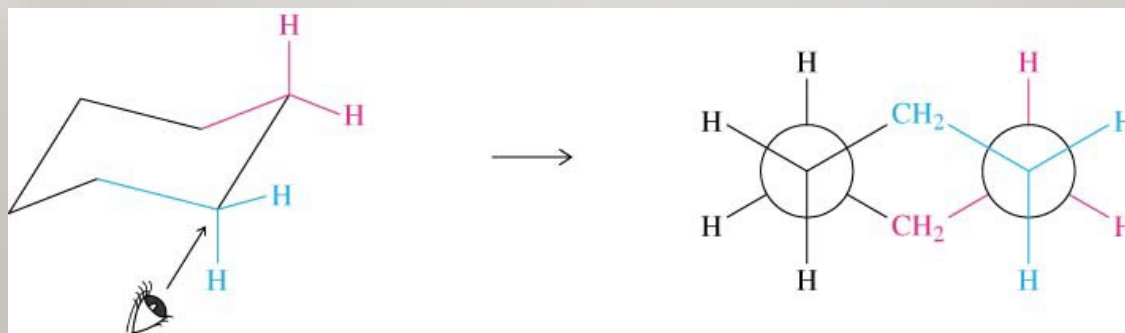
2.3 CYCLOALKANES

The chair conformation of cyclohexane is strain free.

Cyclohexane has several conformations, one of which is called the chair conformation.



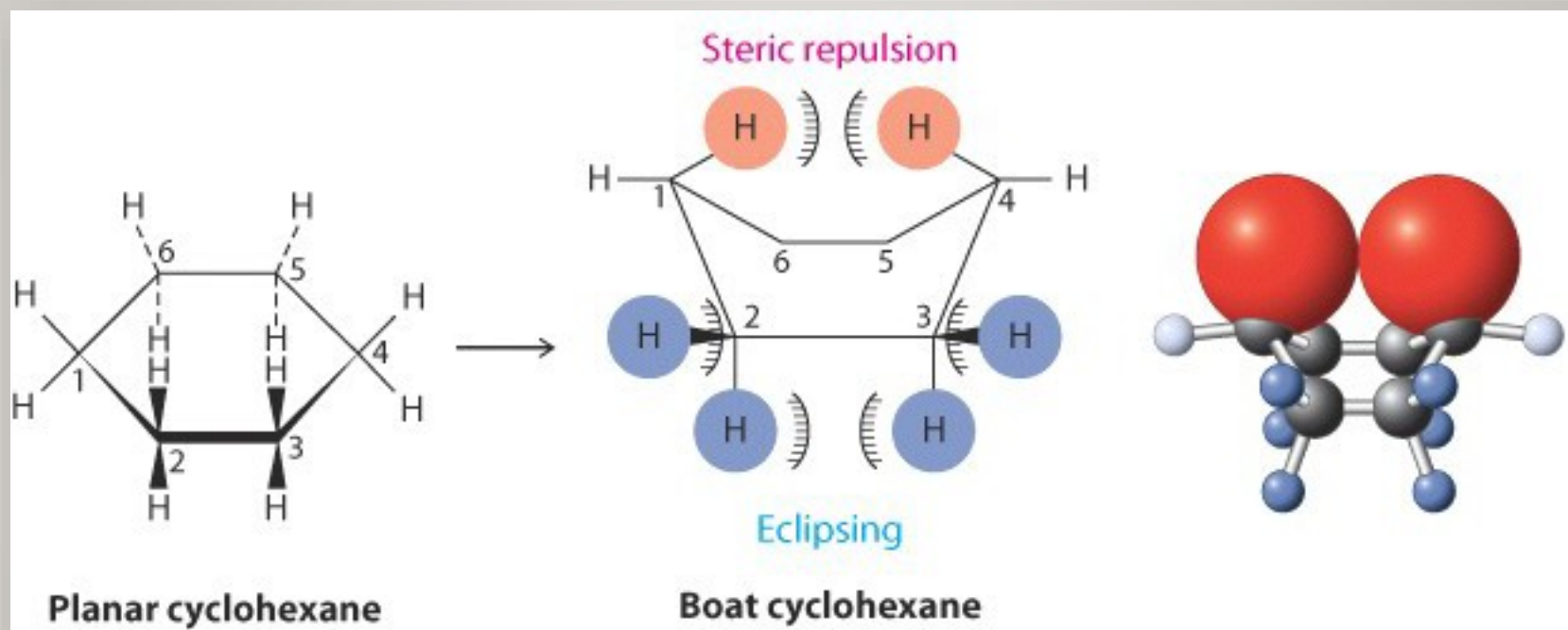
In the chair conformation, eclipsing of the hydrogens is completely prevented, the C-C-C bond angles are very nearly tetrahedral, and the molecule is nearly strain free.



2.3 CYCLOALKANES

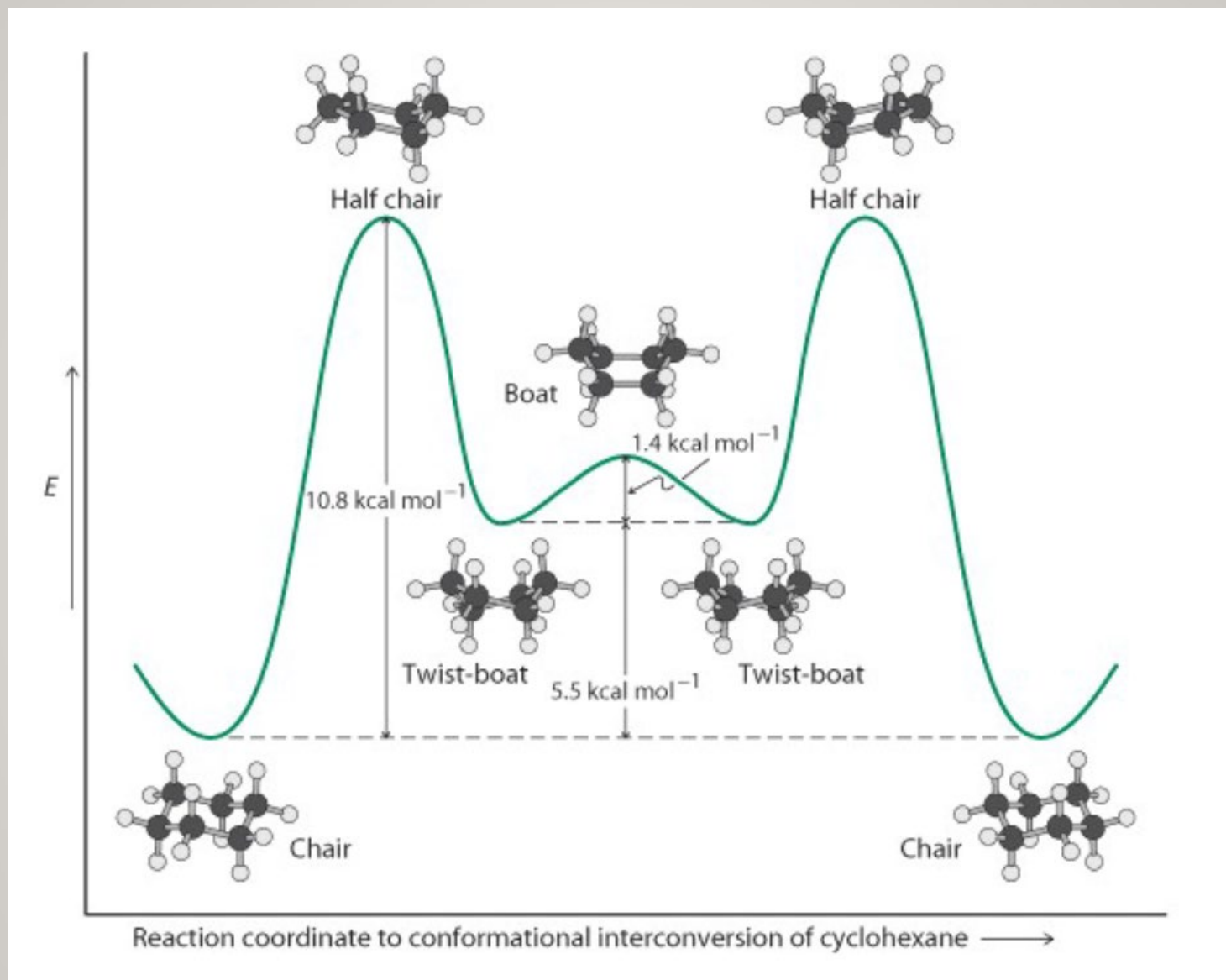
Cyclohexane also has several less stable conformations.

- A second, less stable conformation of cyclohexane is the boat form, which is less stable than the chair form by $6.9 \text{ kcal mol}^{-1}$.



The higher energy is due to the eclipsing of the 8 hydrogens at the base of the boat, and the transannular (steric crowding across a ring) strain between the two hydrogens in the boat framework.

2.3 CYCLOALKANES

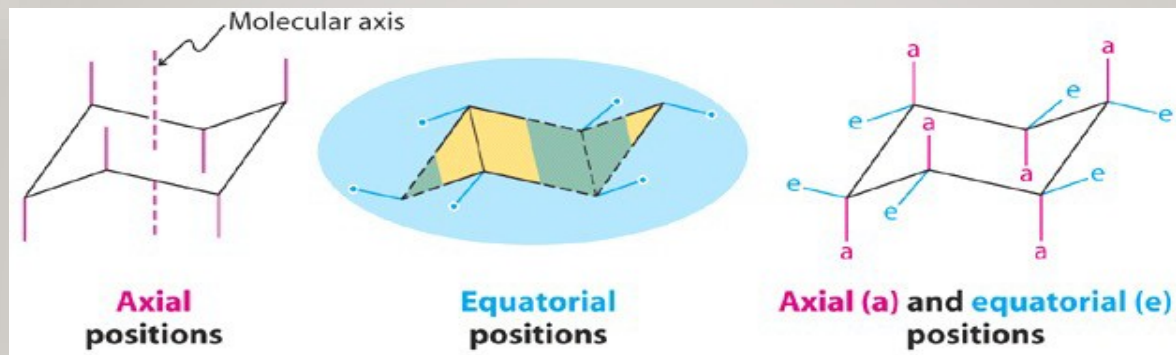


2.3 CYCLOALKANES

Cyclohexane has axial and equatorial hydrogen atoms.

In the chair form, cyclohexane has two types of hydrogens:

- ❑ **Axial** 6 H parallel to the principle molecular axis
- ❑ **Equatorial** 6 H perpendicular to the principle molecular axis



Axial and equatorial methylcyclohexanes are not equivalent in energy.

