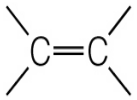
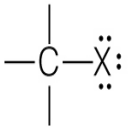
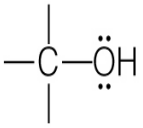
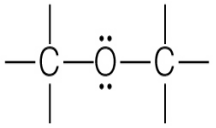
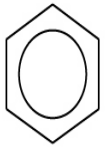
Chapter 4

Alkanes

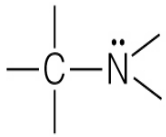
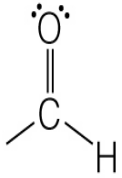
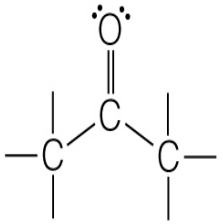
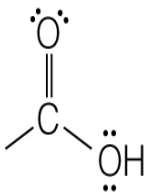
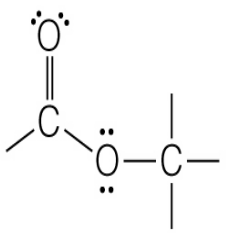
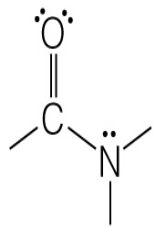
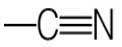
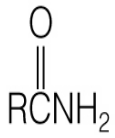
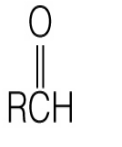
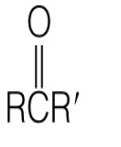
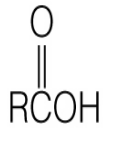
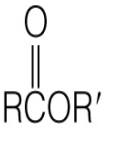
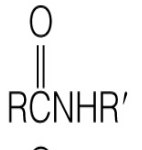
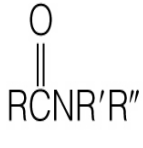
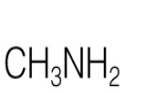
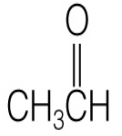
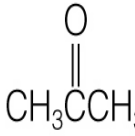
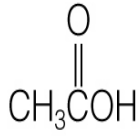
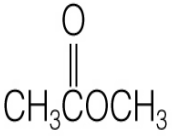
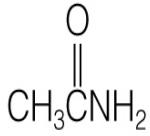
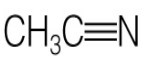
NEPHAR 109 Organic Chemistry
Assist.Prof. Banu Keşanlı

Summary of Important Families of Organic Compounds

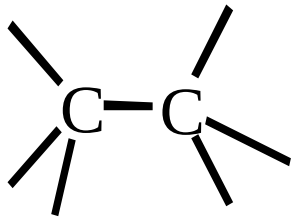
	Family						
	Alkane	**Alkene**	**Alkyne**	**Aromatic**	**Haloalkane**	**Alcohol**	**Ether**
Functional group	C—H and C—C bonds		—C≡C—	Aromatic ring			
General formula	RH	$RCH{=}CH_2$ RCH=CHR $R_2C{=}CHR$ $R_2C{=}CR_2$	RC≡CH RC≡CR	ArH	RX	ROH	ROR
Specific example	CH_3CH_3	$CH_2{=}CH_2$	HC≡CH		CH_3CH_2Cl	CH_3CH_2OH	CH_3OCH_3
IUPAC name	Ethane	Ethene	Ethyne	Benzene	Chloroethane	Ethanol	Methoxymethane
Common name[a]	Ethane	Ethylene	Acetylene	Benzene	Ethyl chloride	Ethyl alcohol	Dimethyl ether

[a]These names are also accepted by the IUPAC.

Summary (cont.)..

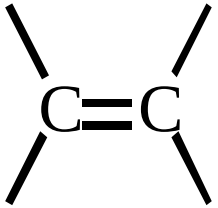
Family						
Amine	**Aldehyde**	**Ketone**	**Carboxylic Acid**	**Ester**	**Amide**	**Nitrile**
						
						
RNH_2 R_2NH R_3N						RCN
						
						
Methanamine	Ethanal	Propanone	Ethanoic acid	Methyl ethanoate	Ethanamide	Ethanenitrile
Methylamine	Acetaldehyde	Acetone	Acetic acid	Methyl acetate	Acetamide	Acetonitrile

General Structure of Alkanes, Alkenes and Alkynes



alkane

(C_nH_{2n+2})



alkene

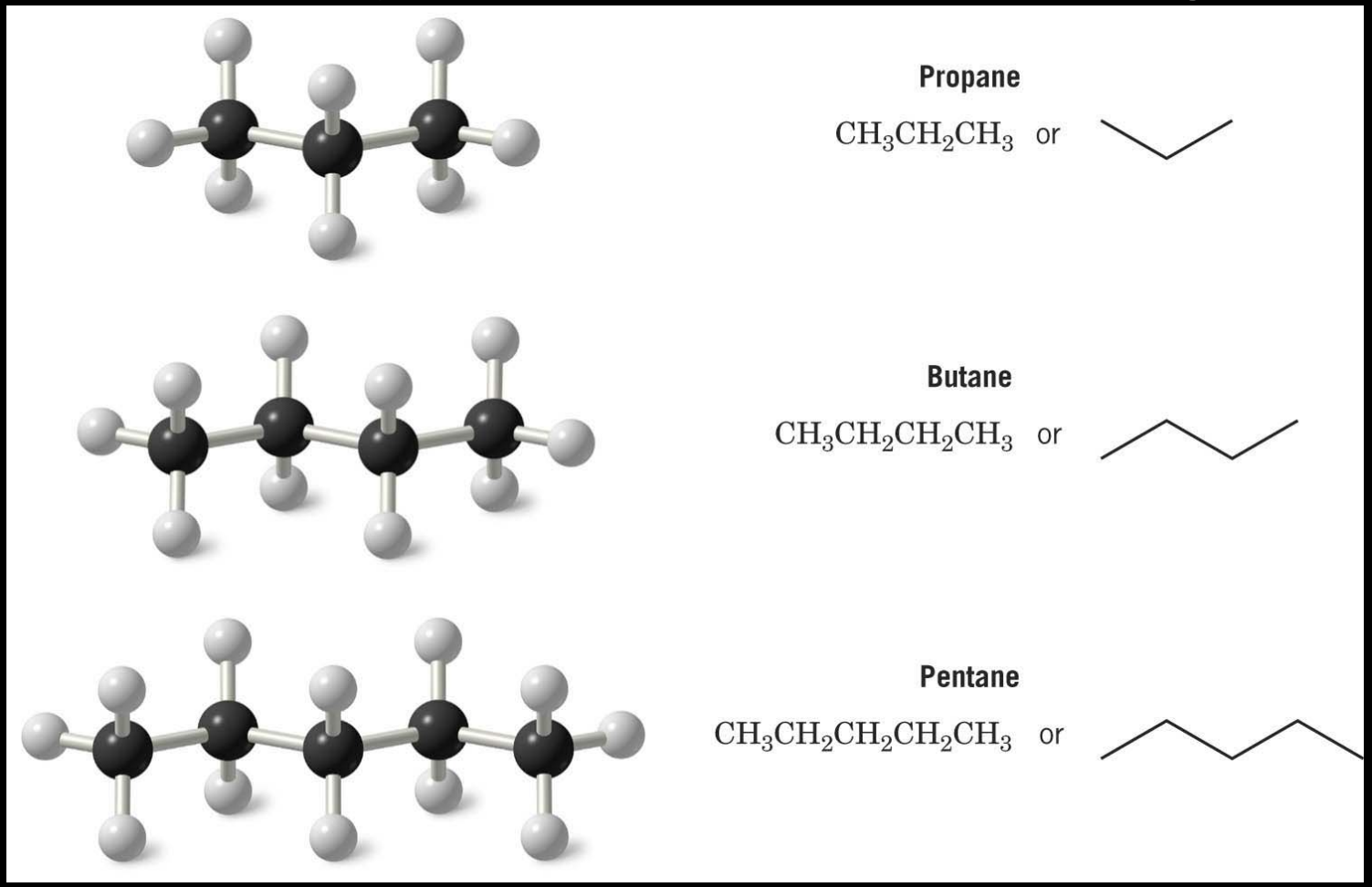
(C_nH_{2n})

alkyne

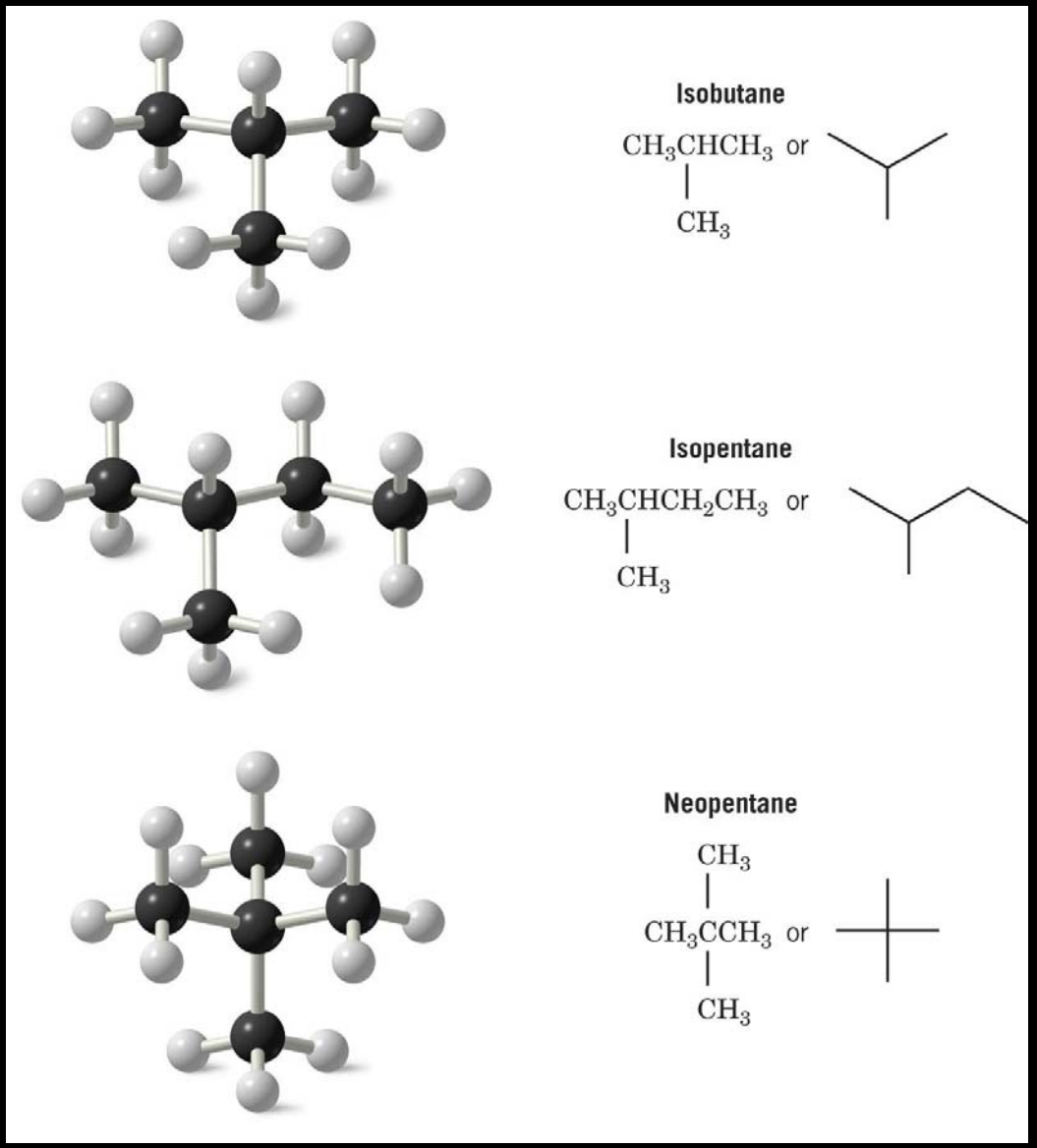
4.2. Shapes of Alkanes

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

- Often described as saturated hydrocarbons as contain only C and H and have C-C single

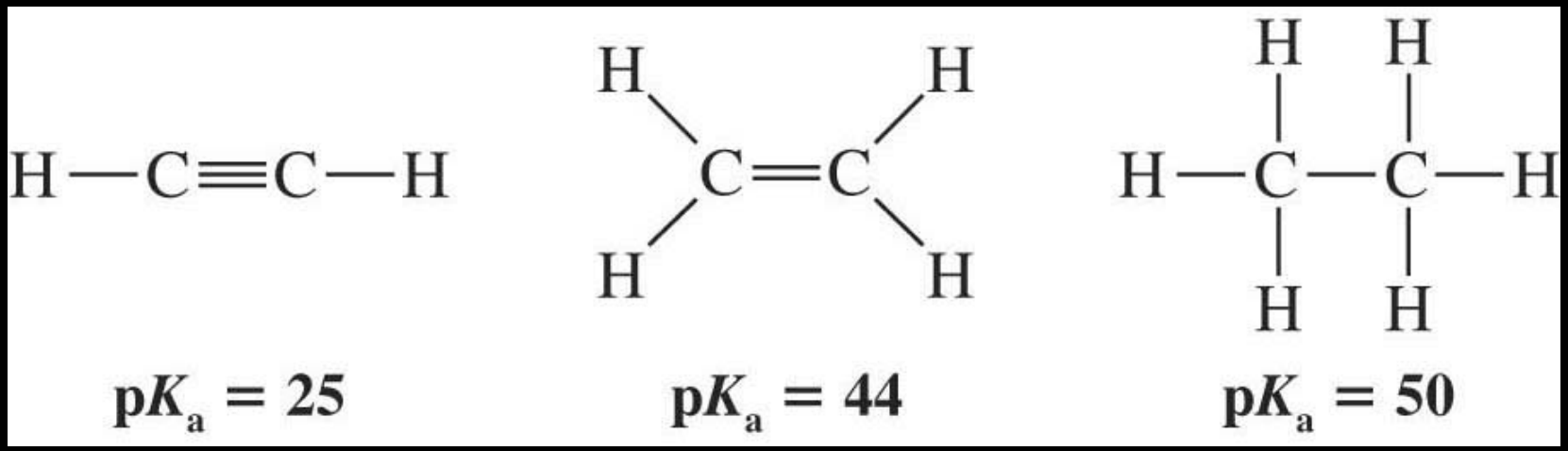


➔**Branched alkanes have at least one carbon which is attached to more than two other carbons**



Acidity Trends

➔Acetylenic hydrogens have a p*K*a of about 25 and are much more acidic than most other C-H bonds



➔The relative acidity of acetylenic hydrogens in solution is:

H—$\ddot{O}$H	>	H—$\ddot{O}$R	>	H—C≡CR	>	H—$\ddot{N}H_2$	>	H—CH=CH_2	>	H—CH_2CH_3
pK_a 15.7		16–17		25		38		44		50

4.3. 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	$CH_3(CH_2)_{98}CH_3$

4.3A 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—

IUPAC Nomenclature

Prefix-Parent-Suffix

Where are the substituents?

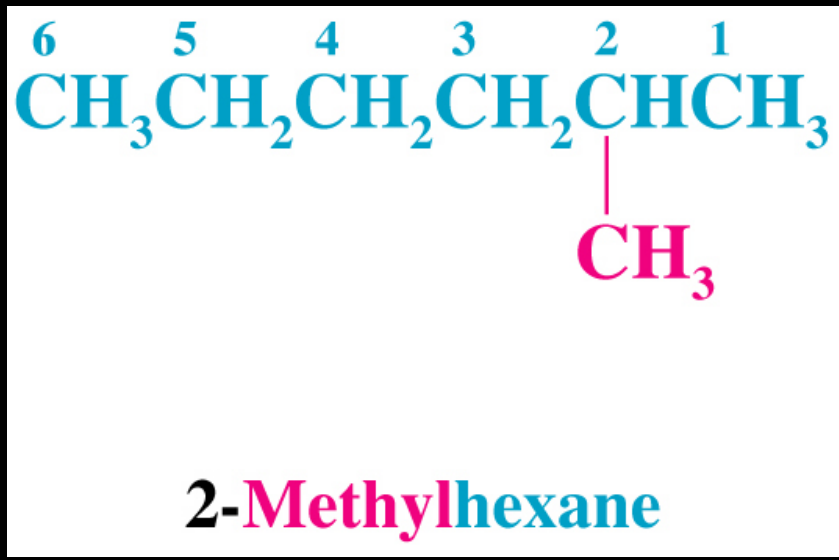
How many carbons?

What family? (functional group)

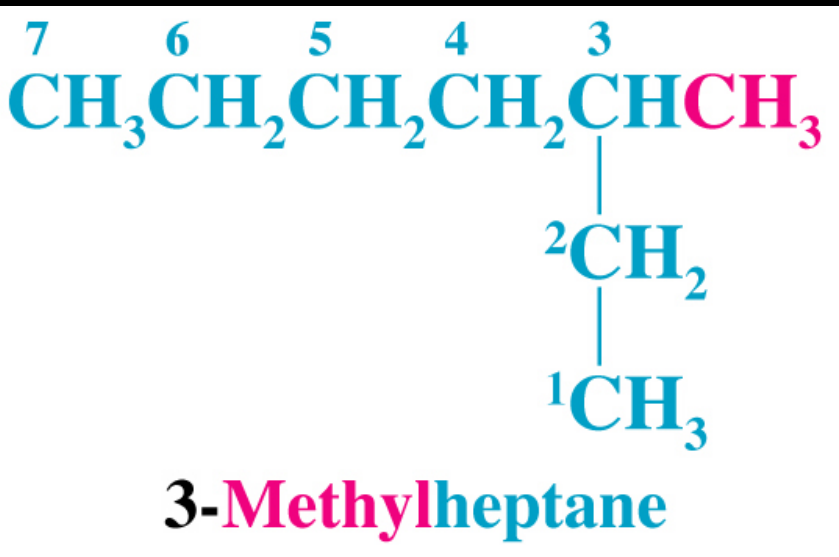
- **If two or more identical substituents are present, use one of the multiplier prefixes *di-, tri-, tetra-*,..**

Nomenclature of Branched-Chain Alkanes (IUPAC)

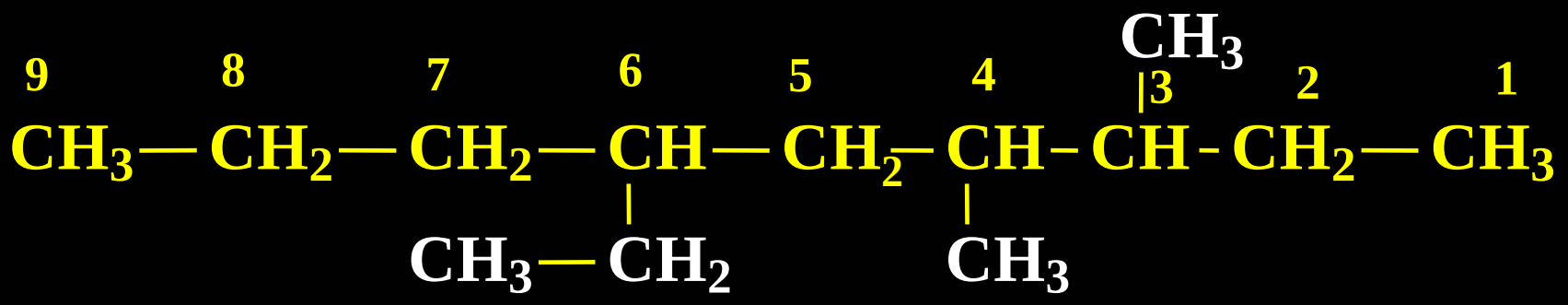
- Locate the longest continuous chain of carbons; this is the parent chain and determines the parent name
- Number the longest chain beginning with the end of the chain nearer the substituent
- Designate the location of the substituent



2-Methylhexane



3-Methylheptane

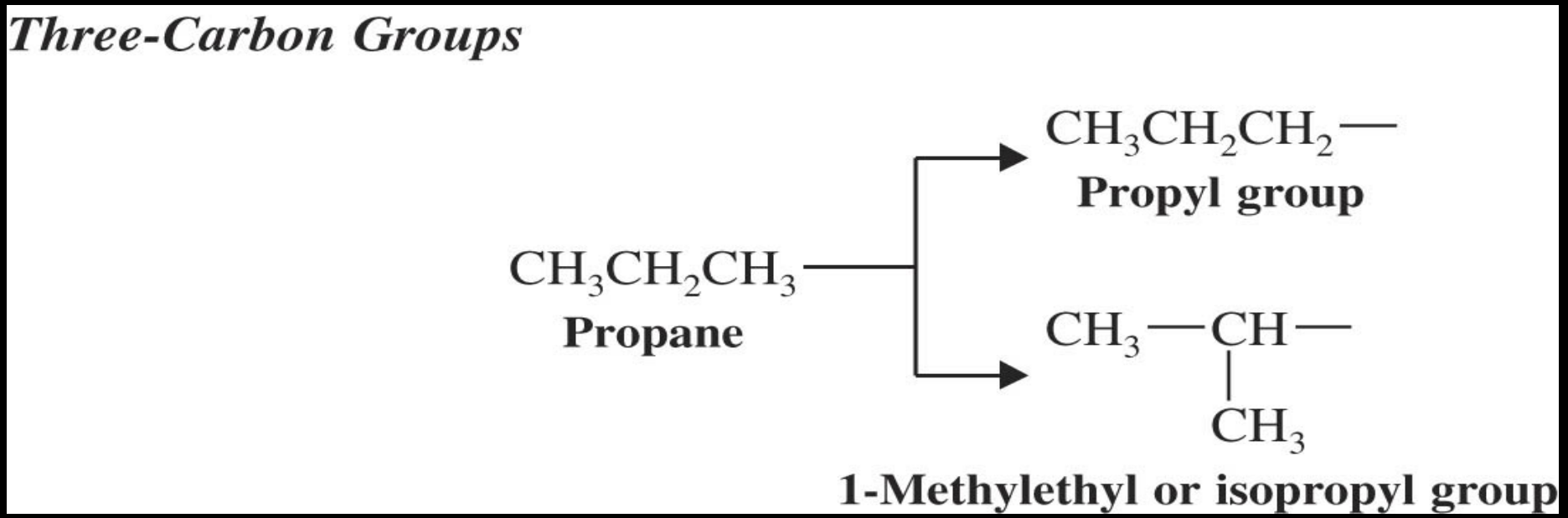


3,4-Dimethyl-6-ethylnonane

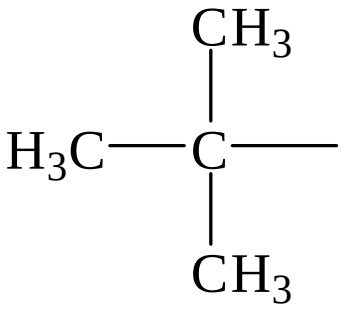
- Location
- Multiplier prefix
- Substituents
- Location
- Parent name
- Functional group

4.3C Nomenclature of Branched Alkyl Chains

➔Two alkyl groups can be derived from **propane**

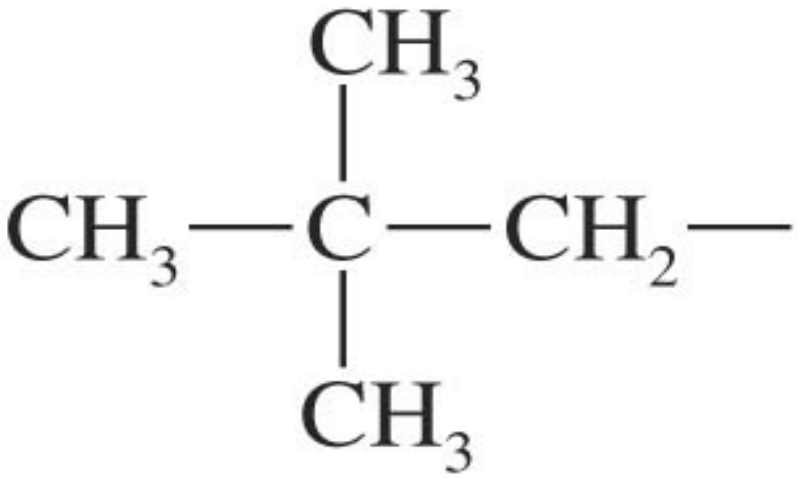


Secondary butyl group (sec-Bu)



Tertiary butyl group (tert-Bu)

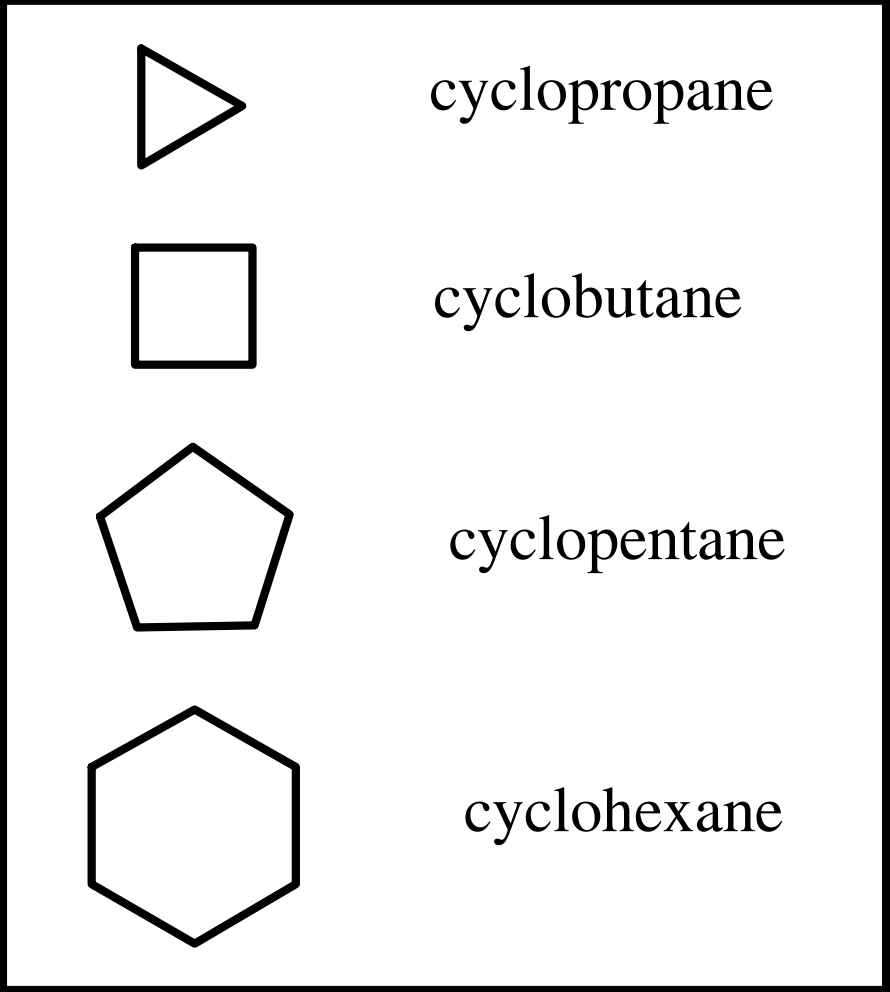
➔**The neopentyl group is a common branched alkyl group**



2,2-Dimethylpropyl or neopentyl group

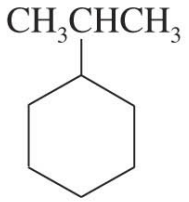
Cycloalkanes

Cycloalkanes are saturated compounds consisting of rings of $-CH_2-$ units with a general formula of $(CH_2)_n$

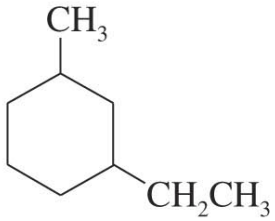


4.4. Nomenclature of Cycloalkanes

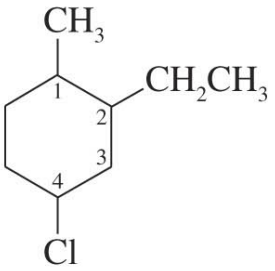
- The prefix cyclo- is added to the name of the alkane with the same number of carbons
  - ➔When one substituent is present it is assumed to be at position one and is not numbered
  - ➔When two alkyl substituents are present the one with alphabetical priority is given position 1
  - ➔Numbering continues 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



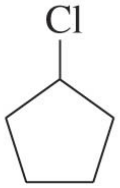
Isopropylcyclohexane



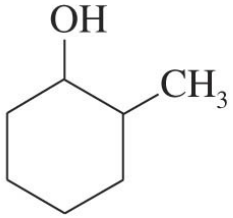
1-Ethyl-3-methylcyclohexane
(*not* 1-ethyl-5-methylcyclohexane)



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

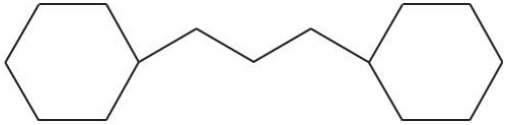


Chlorocyclopentane



2-Methylcyclohexanol

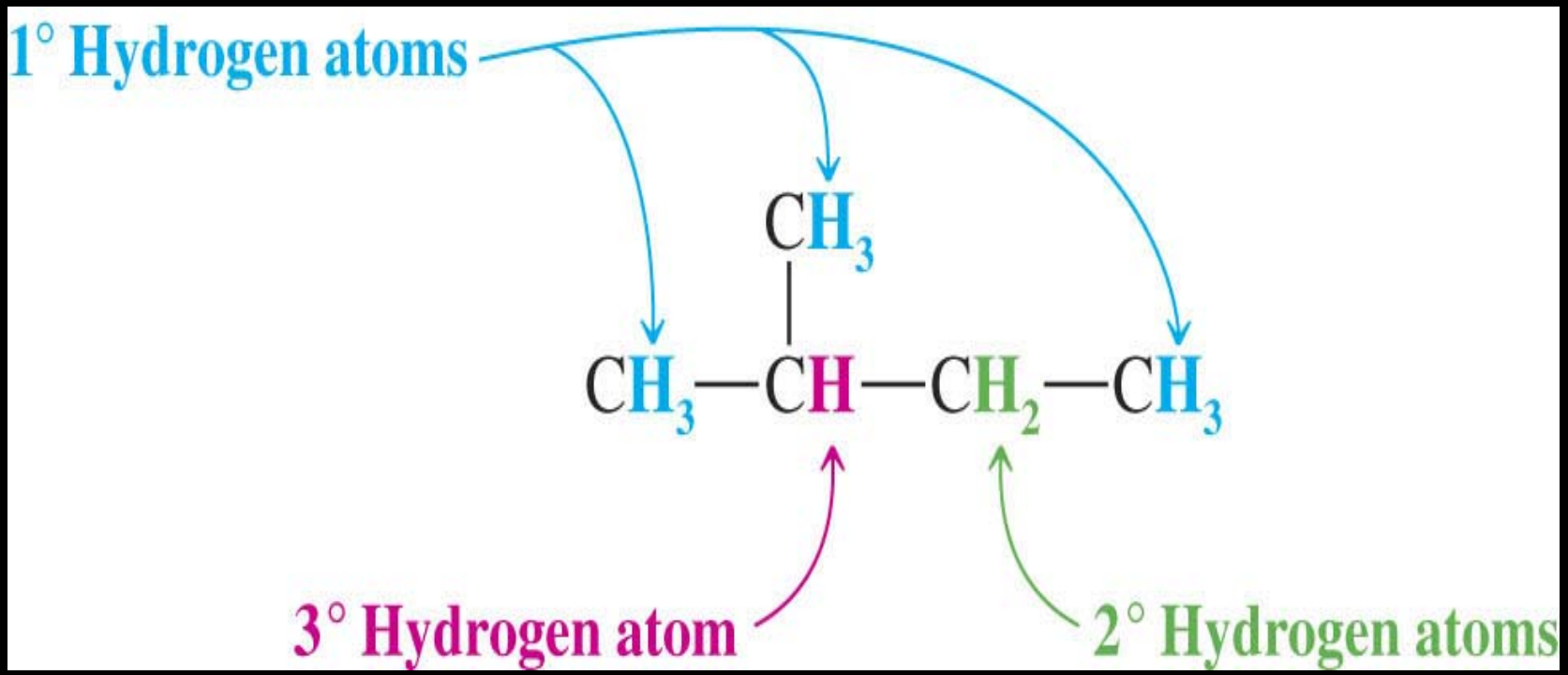
1-Cyclobutylpentane



1,3-Dicyclohexylpropane

4.3D Classification of Hydrogen Atoms

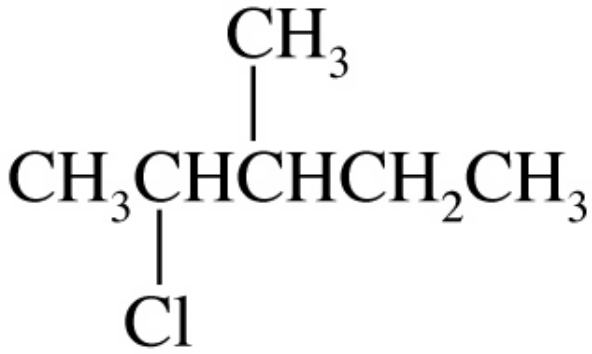
➔Hydrogens take their classification from the carbon they are attached to



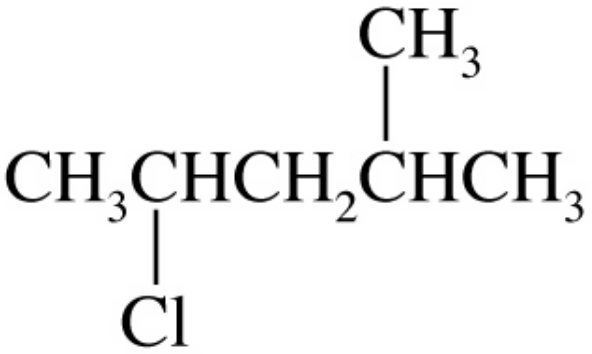
4.3E Nomenclature of Alkyl Halides

➔ **In IUPAC nomenclature halides are named as substituents on the parent chain**

- **Halo and alkyl substituents are considered to be of equal ranking**

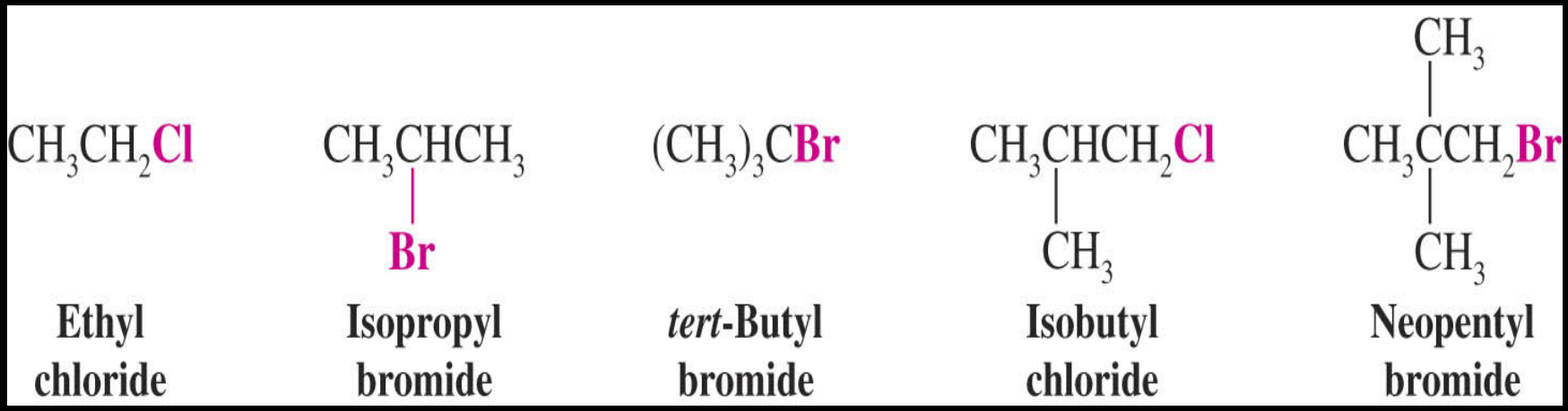


2-Chloro-3-methylpentane



2-Chloro-4-methylpentane

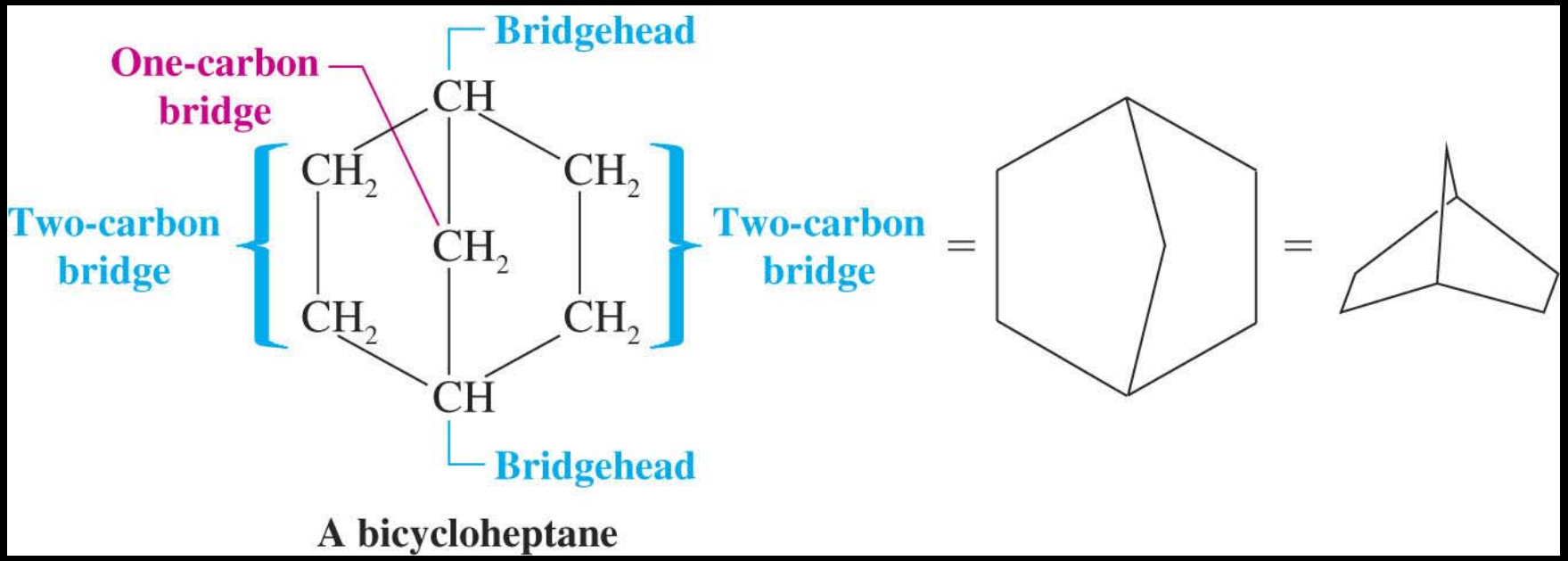
- **Common nomenclature of simple alkyl halides is accepted by IUPAC and still used**



4.4B Bicyclic compounds

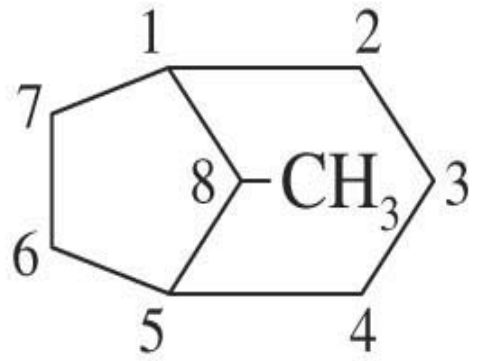
➔Bicyloalkanes contain 2 fused or bridged rings

➔The alkane with the same number of total carbons is used as the parent and the prefix bicyclo- is used

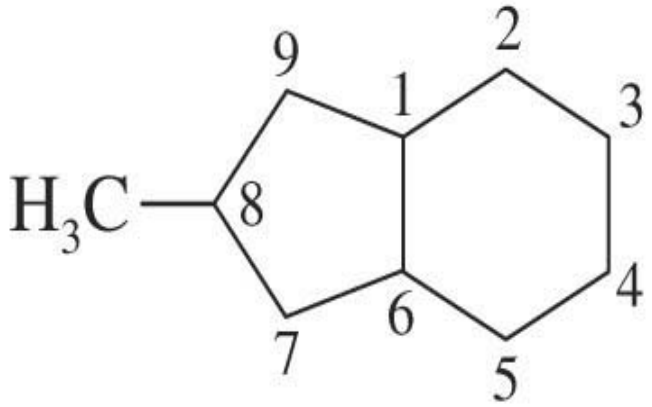


A bicycloheptane

➔**The number of carbons in each bridge is included in the middle of the name in square brackets**



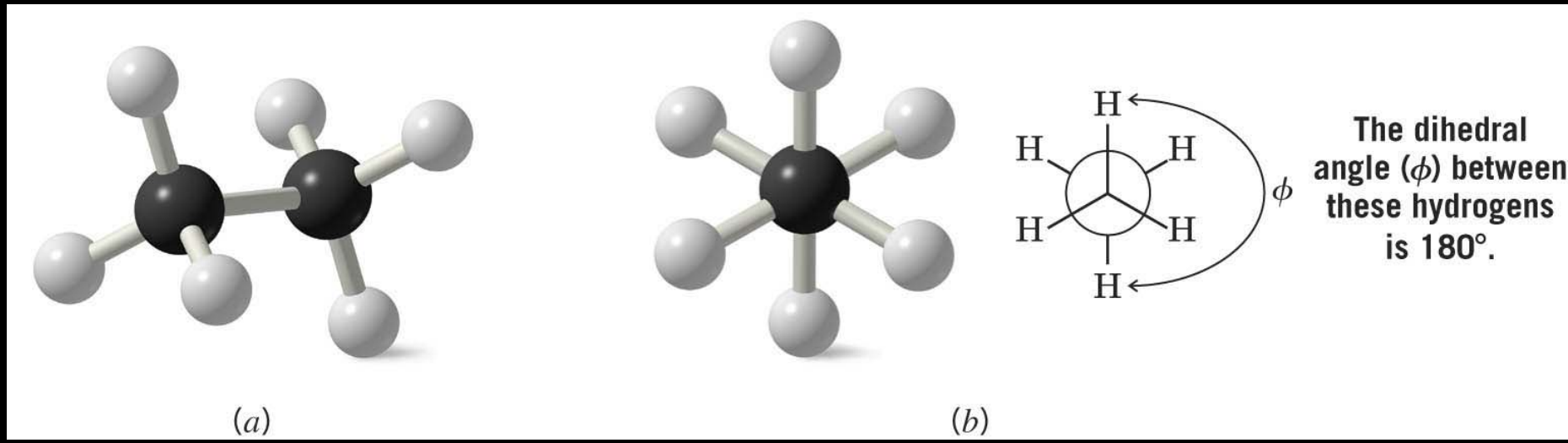
8-Methylbicyclo[3.2.1]octane



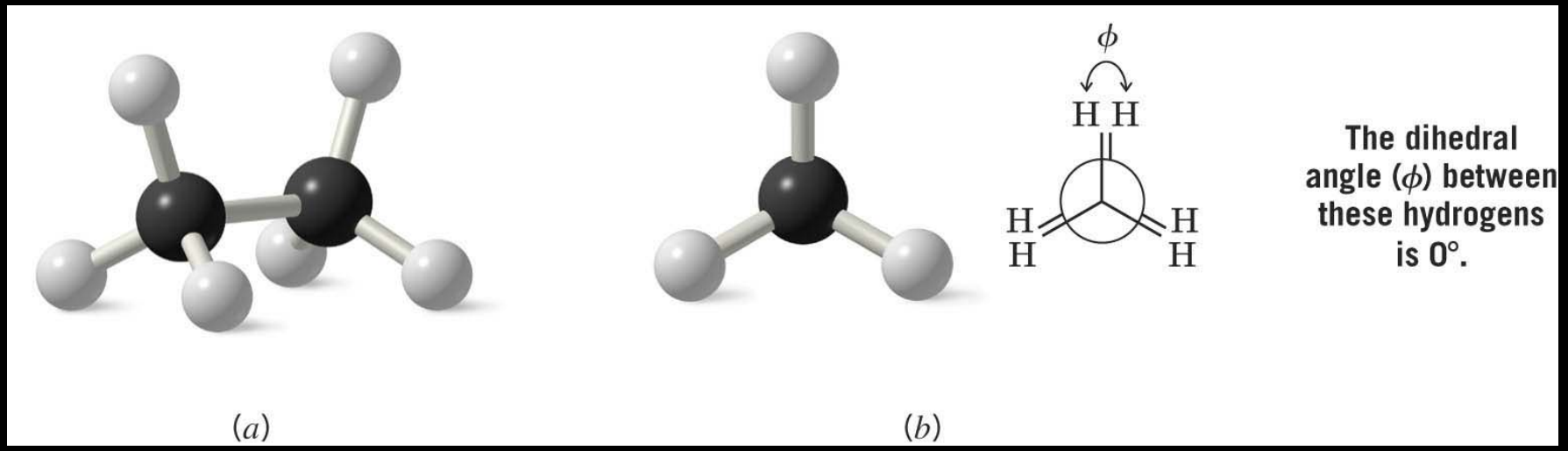
8-Methylbicyclo[4.3.0]nonane

4.8. Sigma Bonds and Bond Rotation

- Ethane has relatively free rotation around the carbon-carbon bond
- The staggered conformation has C-H bonds on adjacent carbons as far apart from each other as possible
  - The drawing to the right is called a Newman projection



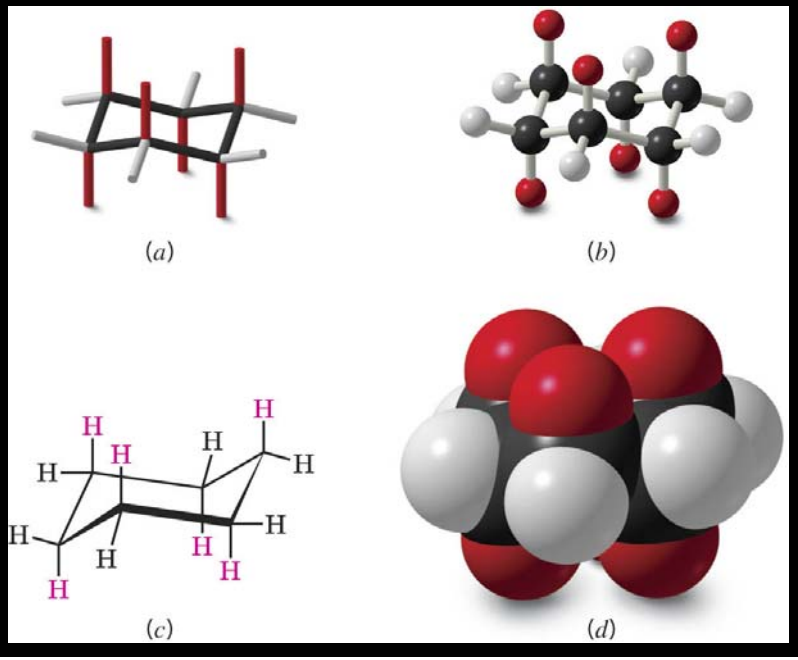
➔**The eclipsed conformation has all C-H bonds on adjacent carbons directly on top of each other**

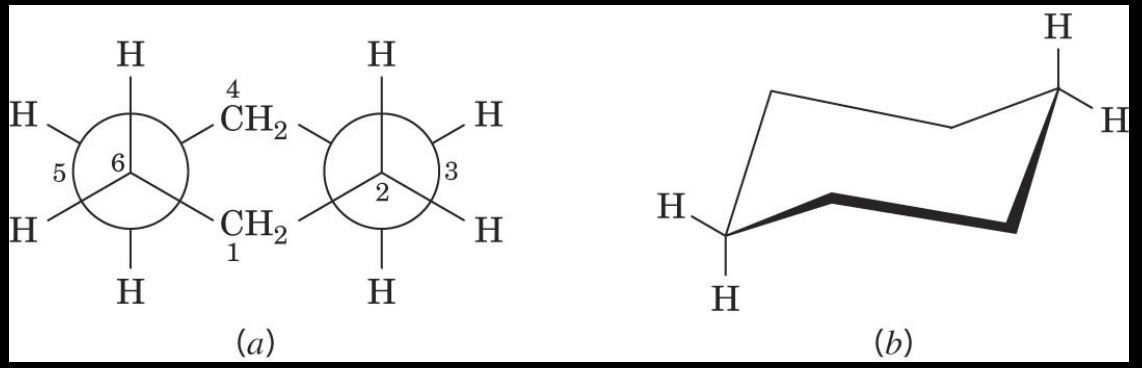


4.12 Conformations of Cyclohexane

➔**The chair conformation has no ring strain**

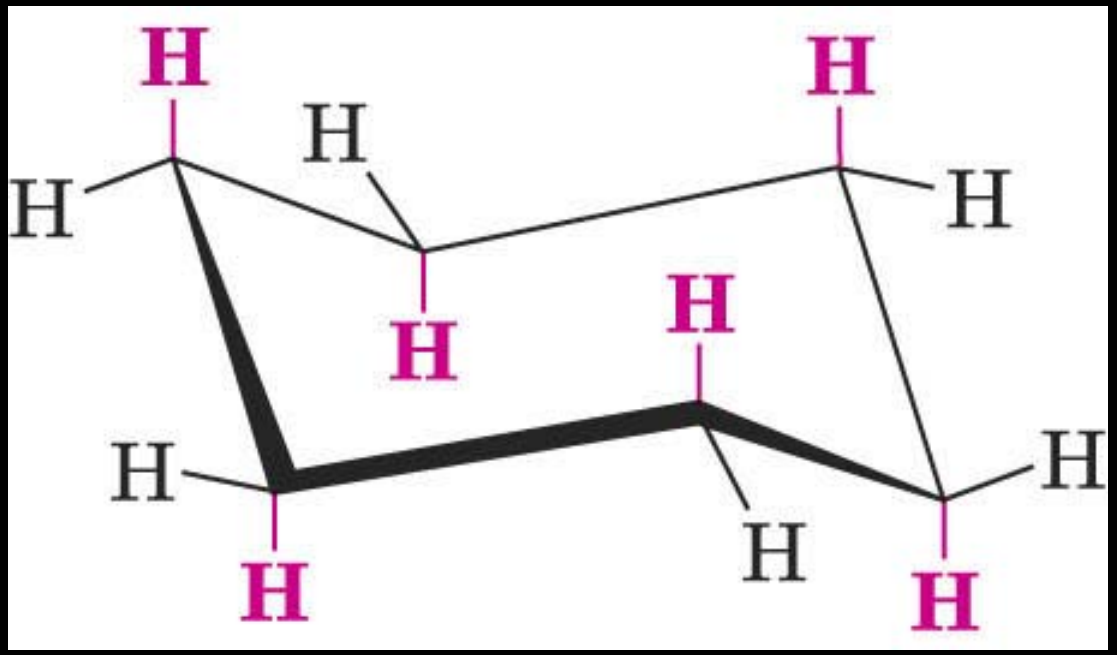
- **All bond angles are 109.5° and all C-H bonds are perfectly staggered**



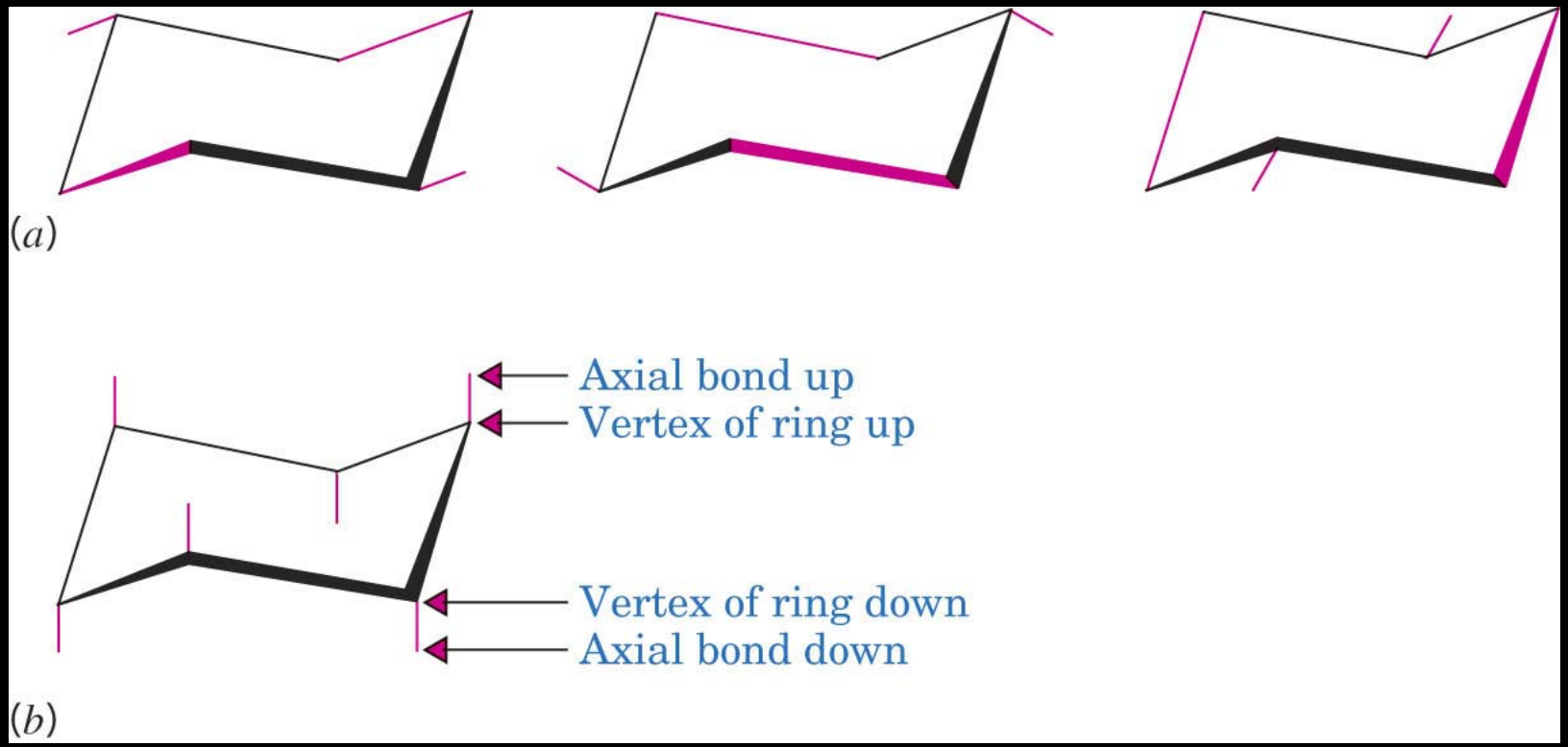


4.13 Substituted Cyclohexanes: Axial and Equatorial Hydrogen Atoms

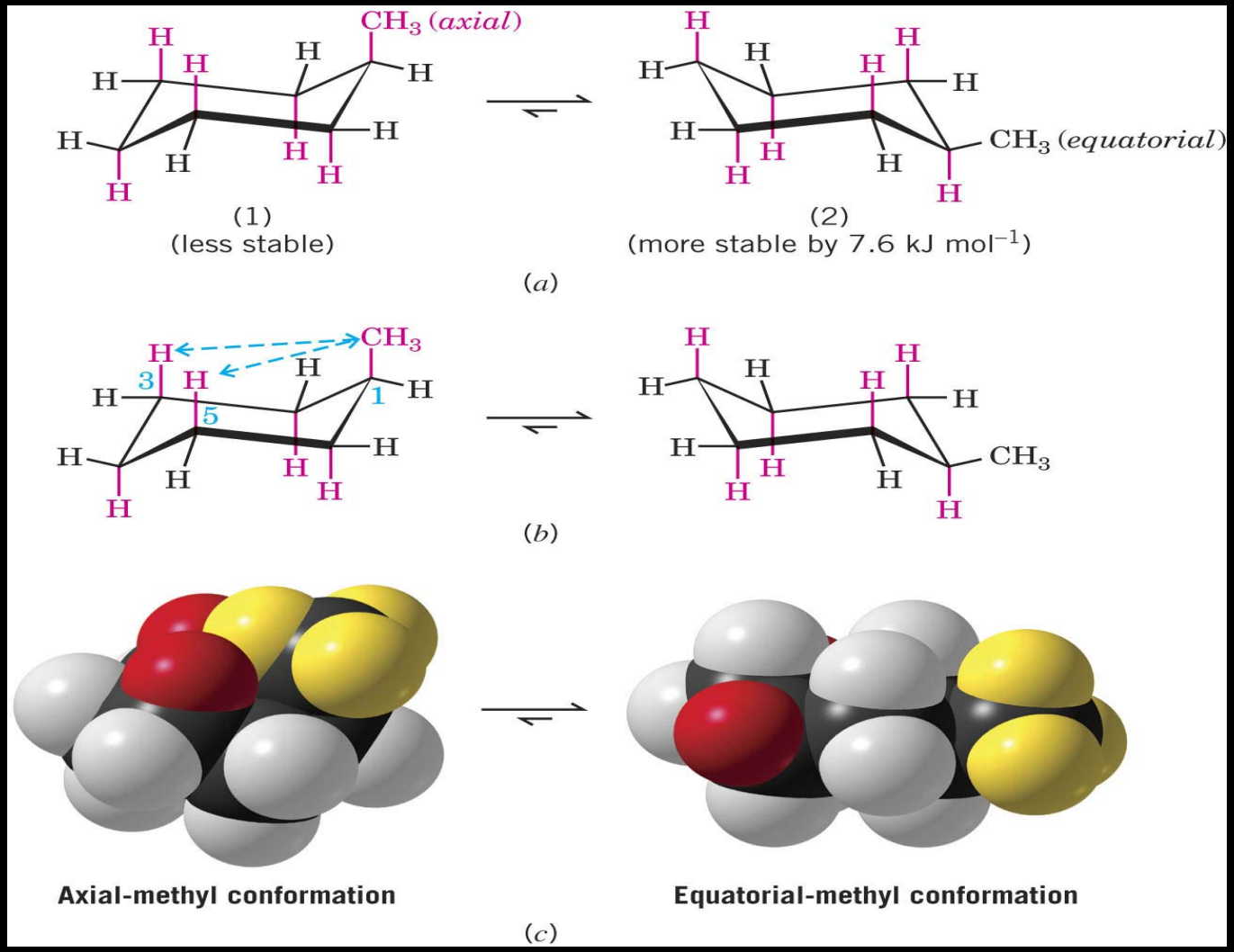
- Axial hydrogens are perpendicular to the average plane of the ring
- Equatorial hydrogens lie around the perimeter of the ring



- **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**



➔Methyl cyclohexane is more stable with the methyl equatorial as the axial methyl has an unfavorable 1,3-diaxial interaction with axial C-H bonds 2 carbons away

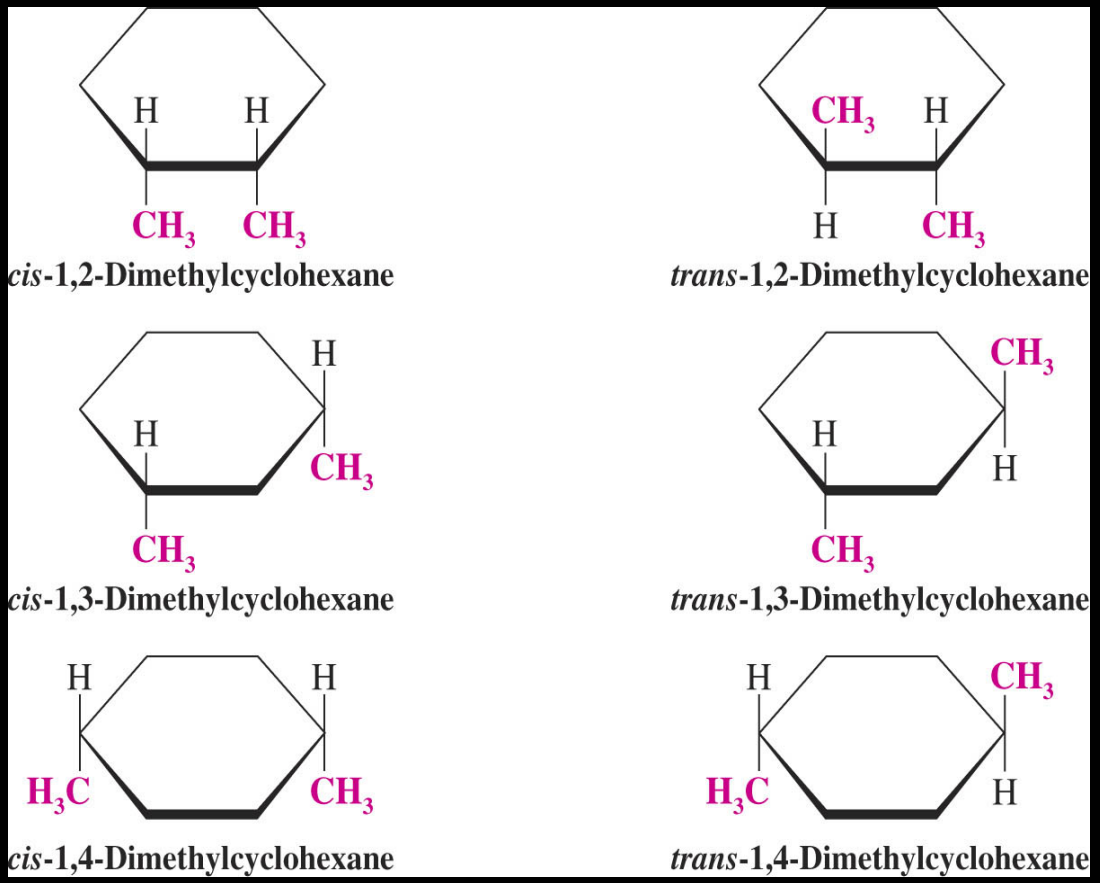


4.14 Disubstitued Cycloalkanes

➔Can exist as pairs of cis-trans stereoisomers

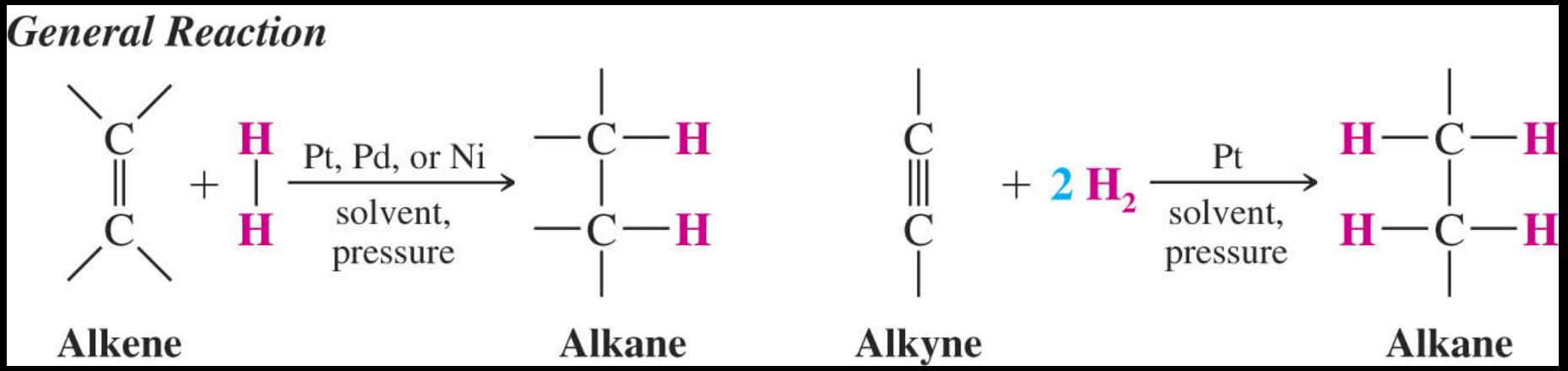
Cis: groups on same side of ring

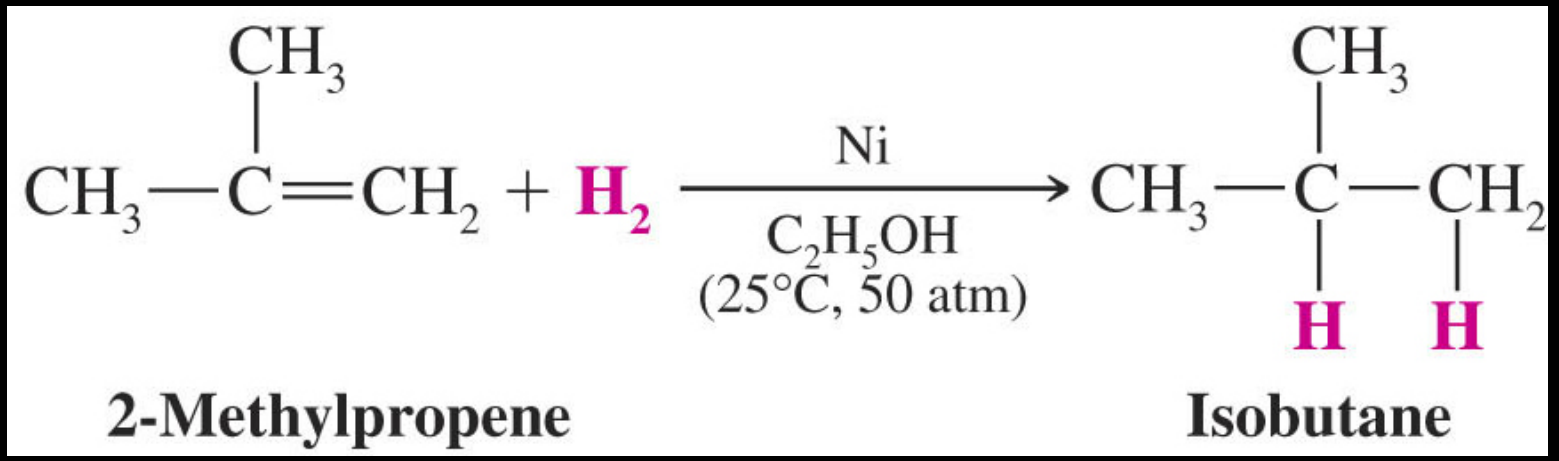
Trans: groups on opposite side of ring



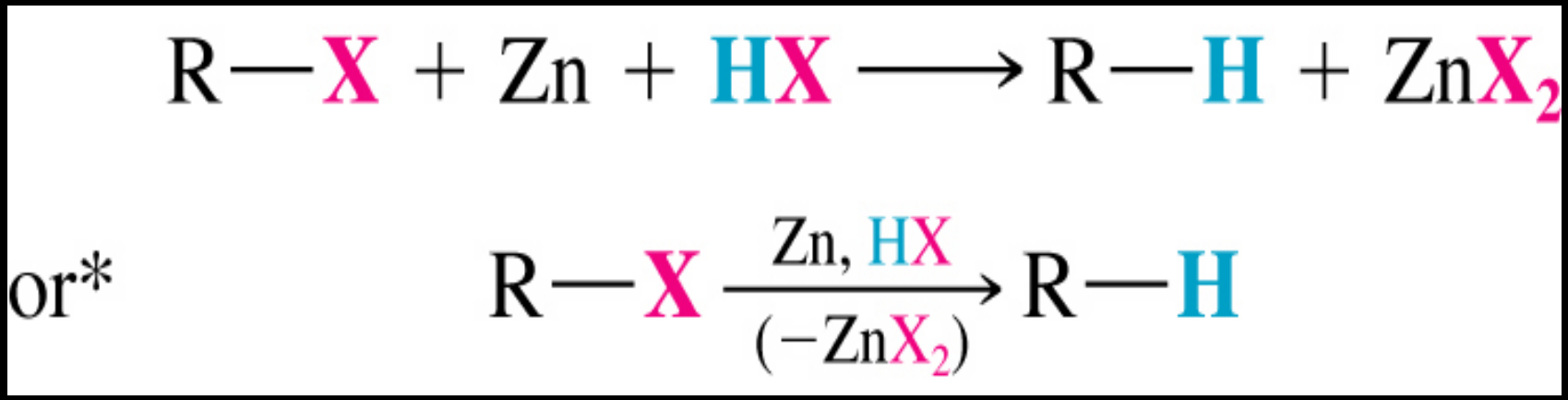
4.18 Synthesis of Alkanes

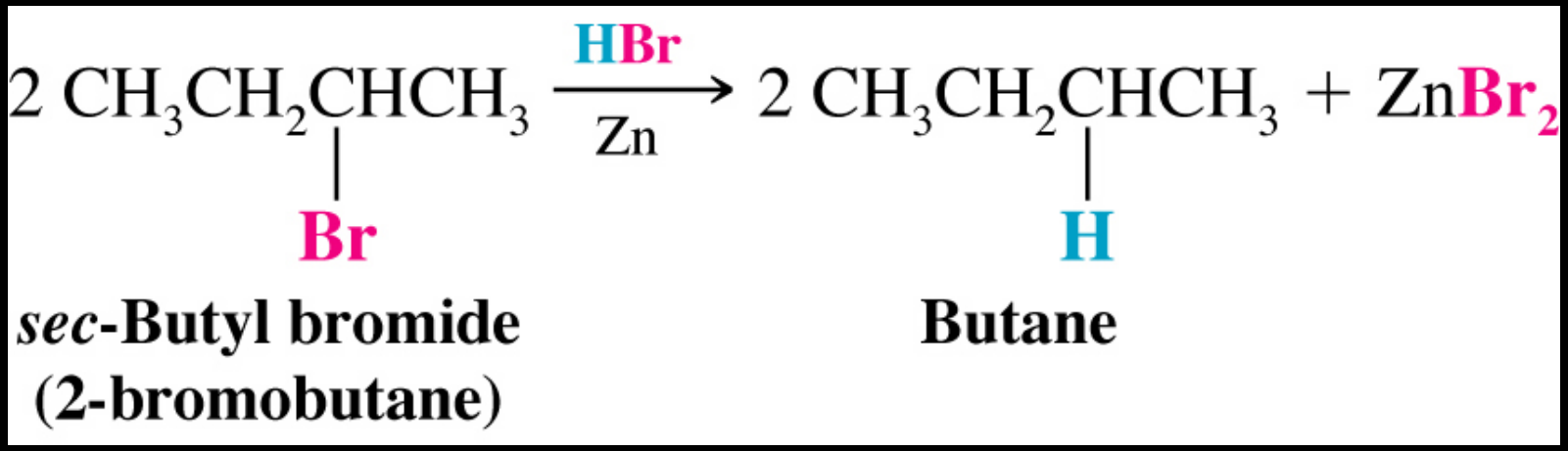
- **Hydrogenation of Alkenes and Alkynes**





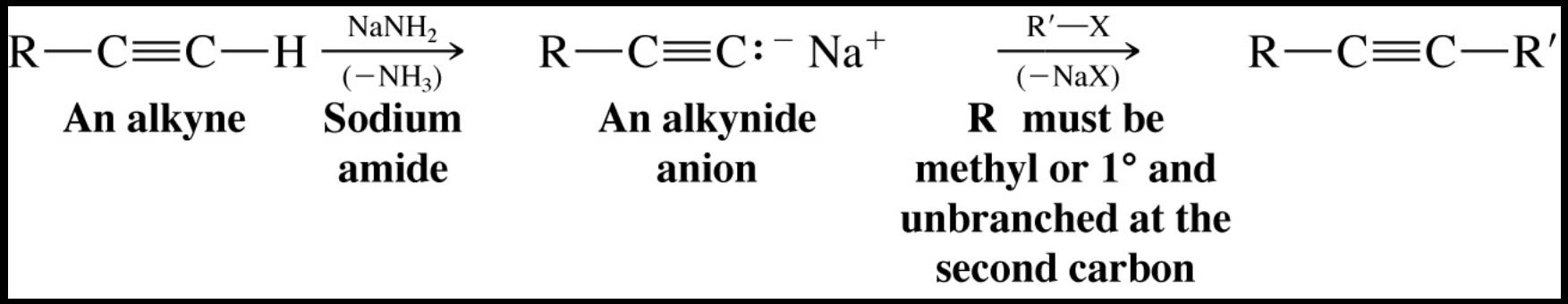
4.18A Reduction of Alkyl Halides

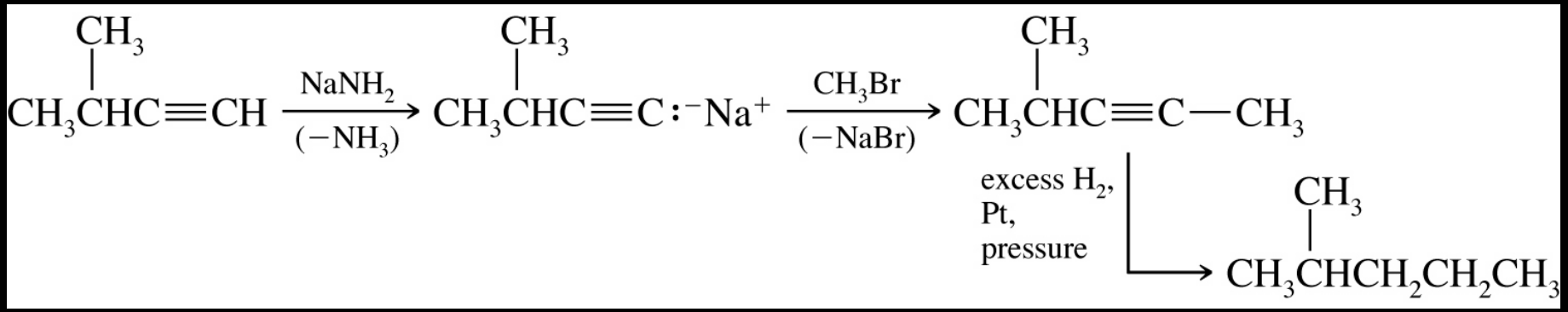




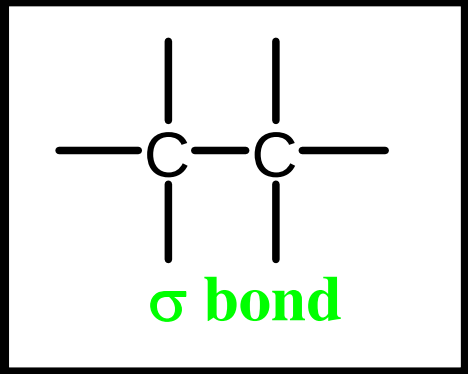
4.18C Alkylation of Terminal Alkynes

➔Alkynes can be subsequently hydrogenated to alkanes





Reactivity of Alkanes



- Alkanes have strong C-C, C-H bonds
- Show slight affinity for chemical reactions

Combustion Reaction

$$CH_4 + 2O_2 \longrightarrow 2CO_2 + 2H_2O + 890kJ/mol$$

Halogenation under UV light

$$CH_4 + Cl_2 \xrightarrow{h\nu} \longrightarrow CCl_4 + HCl$$