

Alkanes

Chapters 3, 4, 10.2, 10.4
Organic Chemistry, 8th Edition
John E. McMurry

Hydrocarbons

❑ **Aliphatic** (Αλειφαρ = Ointment).

- **Alkanes** (saturated hydrocarbons): hydrocarbons having only single C–C and C–H bonds.
 - Linear (*normal* alkanes, *n*-alkanes)
 - Branched
 - Cyclic
- **Alkenes** (olefins): hydrocarbons having double bonds.
- **Alkynes**: hydrocarbons having triple bonds.

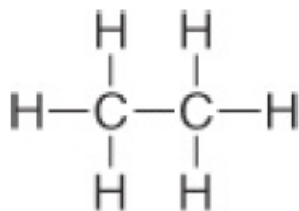
❑ **Aromatic**

Alkanes

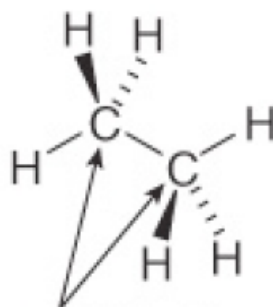
Number of C-atoms	Molecular formula	Name (<i>n</i> -alkane)
1	CH ₄	methane
2	C ₂ H ₆	ethane
3	C ₃ H ₈	propane
4	C ₄ H ₁₀	butane
5	C ₅ H ₁₂	pentane
6	C ₆ H ₁₄	hexane
7	C ₇ H ₁₆	heptane
8	C ₈ H ₁₈	octane
9	C ₉ H ₂₀	nonane
10	C ₁₀ H ₂₂	decane
20	C ₂₀ H ₄₂	eicosane

Empirical formula: C_nH_{2n+2}

Ethane

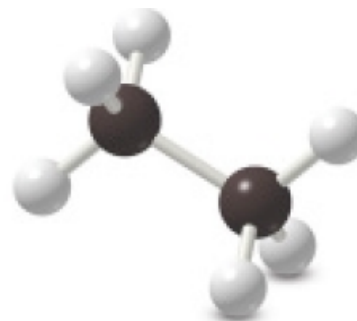


ethane

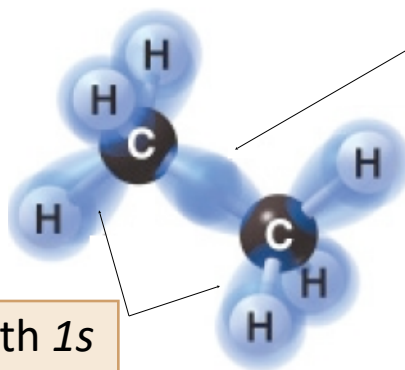


tetrahedral sp^3 C

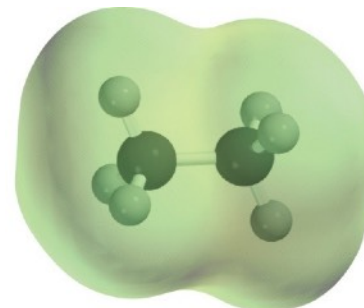
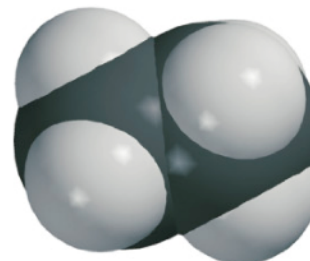
=



Two sp^3 hybrids overlap giving the C-C σ bond

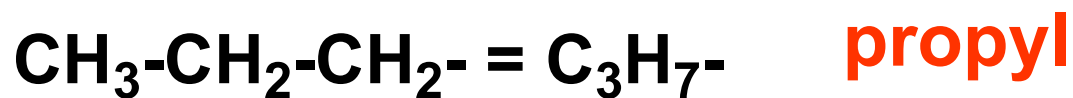
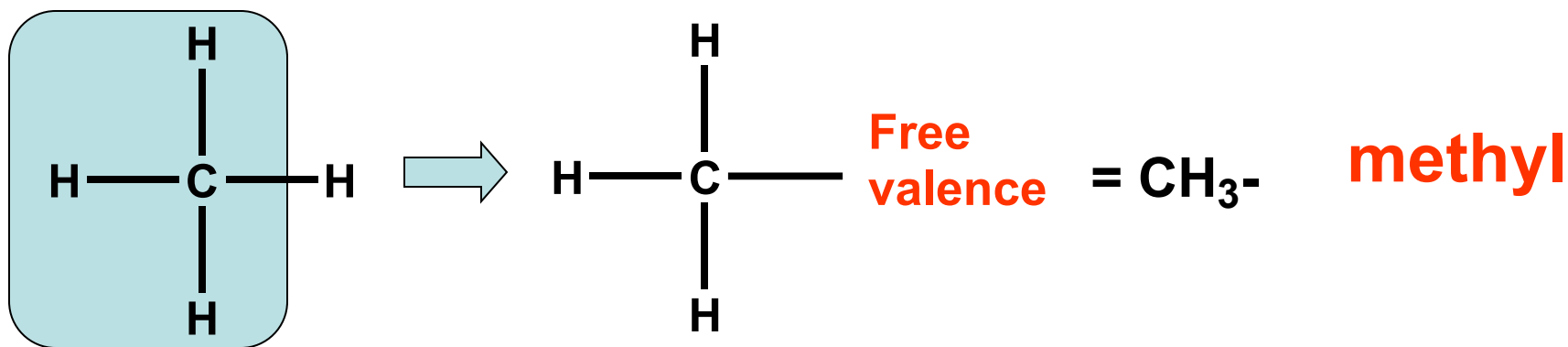


sp^3 hybrids on C overlap with $1s$ orbitals on H giving the C-H σ bonds.



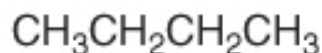
Alkyl Groups

Root-Suffix (= yl)

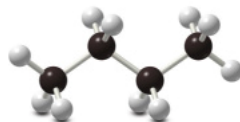


Alkanes – Structural Isomerism

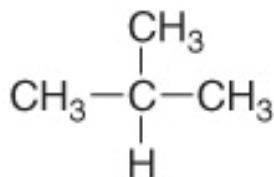
- ❑ There are two hydrocarbons with empirical formula C_4H_{10} : butane and isobutane.
- ❑ Butane and isobutane are structural isomers: they have the same composition but different physico-chemical properties.



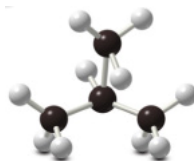
butane



Linear Alkane

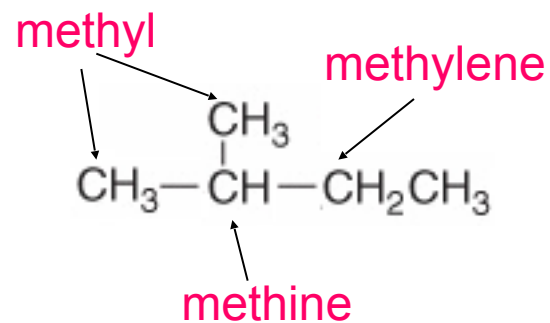
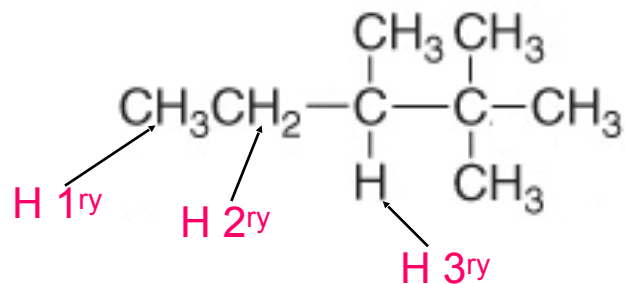
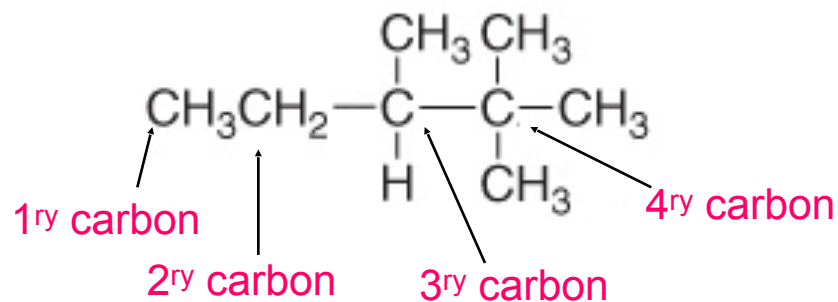


isobutane

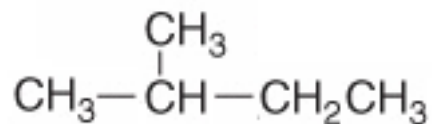


Branched Alkane

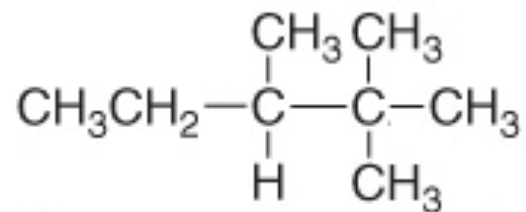
Examples



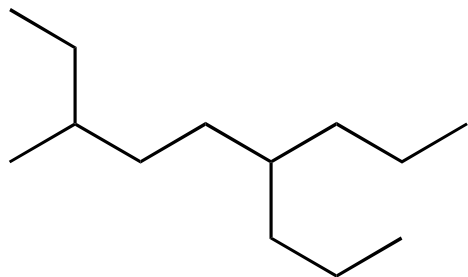
Nomenclature



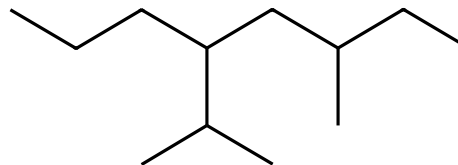
2-methylbutane



2,2,3-trimethylpentane



3-methyl-6-propylnonane



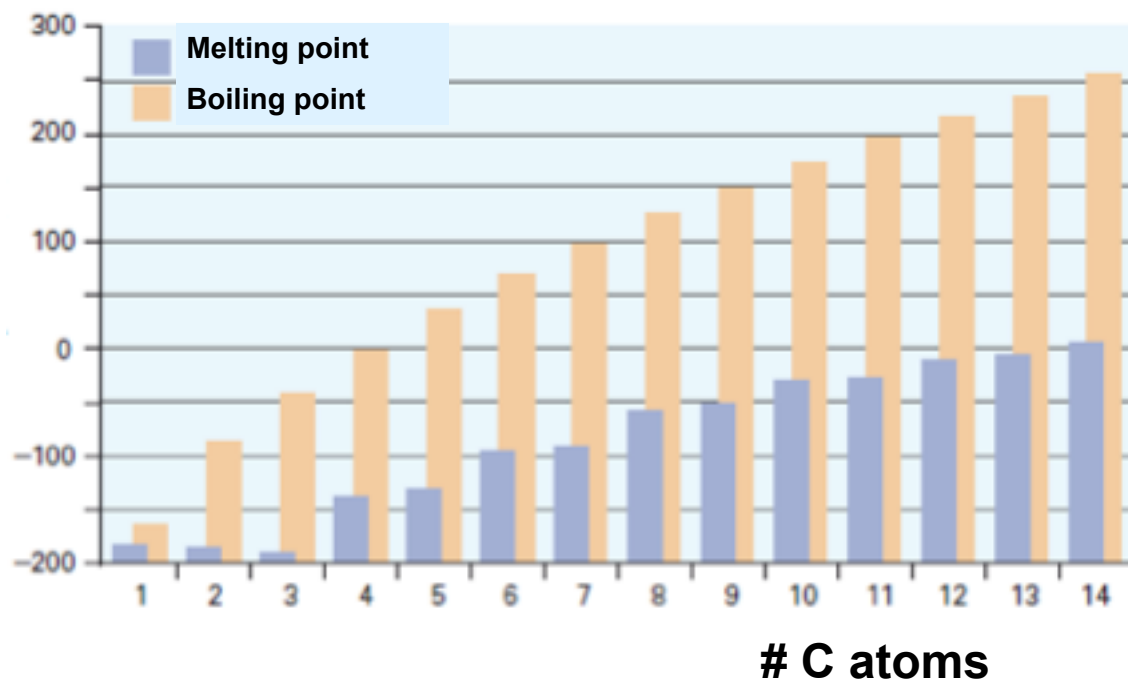
5-(1-methylethyl)-3-methyloctane

Alkyl Groups

C-Atoms	Structure	Name	C-Atoms	Structure	Name
1	CH_3-	methyl	5	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$	<i>n</i> -pentyl
	$-\text{CH}_2-$	methylene		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2-$	isopentyl
	$-\text{CH}-$	methine		$\text{CH}_3\text{C}(\text{CH}_3)_2\text{CH}_2-$	neopentyl
2	CH_3CH_2-	ethyl		$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	sec-pentyl
3	$\text{CH}_3\text{CH}_2\text{CH}_2-$	<i>n</i> -propyl		$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	
	$\text{CH}_3\text{CH}(\text{CH}_3)-$	isopropyl			
4	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$	<i>n</i> -butyl			
	$\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2-$	isobutyl			
	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)-$	sec-butyl			
	$\text{CH}_3\text{C}(\text{CH}_3)_2-$	<i>tert</i> -butyl			

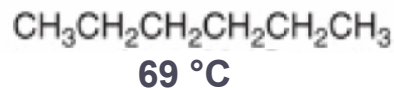
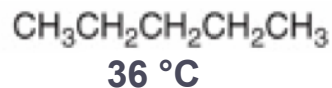
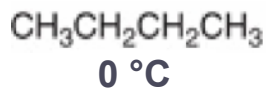
Physical Properties

Temperature

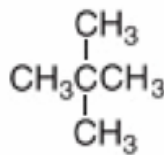


Physical Properties

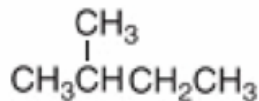
b.p.



Surface area increases with C-atoms



10 °C



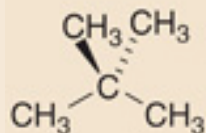
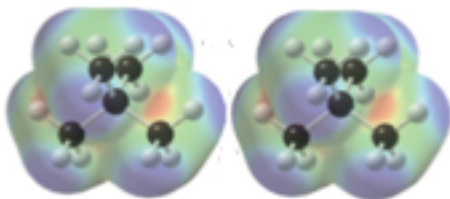
30 °C



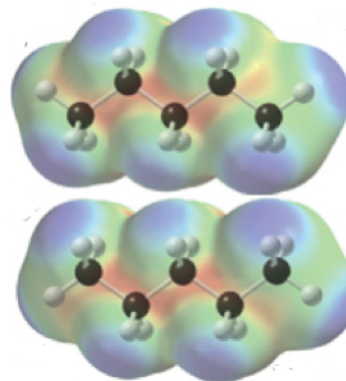
36 °C

Surface area decreases with branching

Compact,
spherical:
weaker
interactions



neopentane
b.p. 10 °C



Long,
cylindrical:
stronger
interactions

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
n-pentane
b.p. 36 °C

Physical Properties

Physical state: C1-C4 gas /b.p. -160° - 0°
 C5-C17 liq./m.p. -130° - 20°
 >C17 solid

Solubility: soluble in organic solvents (apolar)
 insoluble in water

Natural Sources

Natural sources of alkanes are natural gas and oil.

Natural gas contains mainly methane: minor components are ethane, propane and butane.

Oil is a complex mixture of, mainly, C_1 - C_{40} hydrocarbons.

Distillation of crude oil (refining) separates oil in fractions with different boiling point. The main fractions are:

gasoline: C_5H_{12} – $C_{12}H_{26}$

kerosene: $C_{12}H_{26}$ – $C_{16}H_{34}$

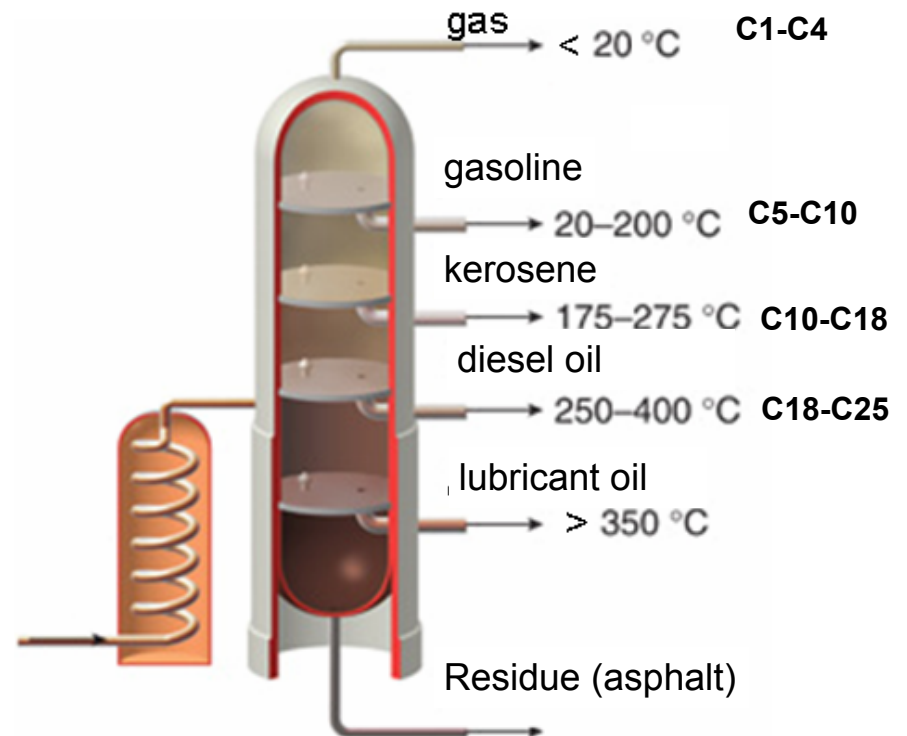
diesel oil: $C_{15}H_{32}$ – $C_{18}H_{38}$

Refining

- ❑ In the refining process, crude oil is heated and the volatile fractions distill first, followed by fractions with higher boiling points.



Pre-heated crude oil and gases



Industrial Treatments of Refined Oil

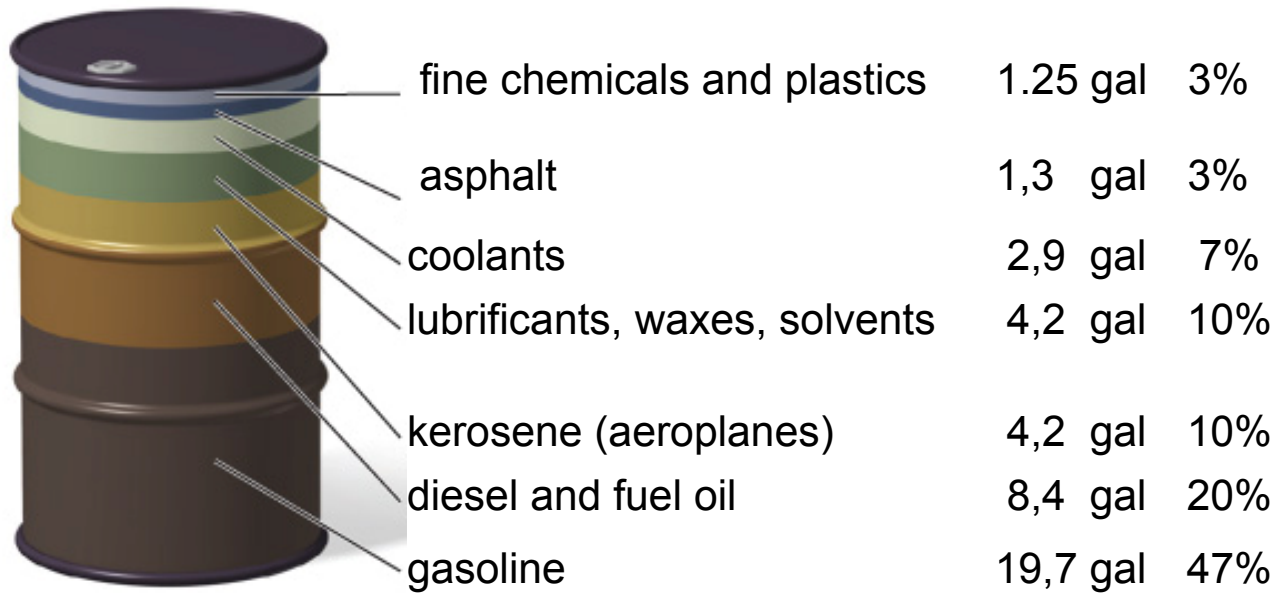
❑ Cracking (kerosene, diesel oil)

- Converts high MW hydrocarbons in lower MW hydrocarbons (hydrocracking).
- Converts alkanes in alkenes (intermediates for the fine chemical industry).

❑ Reforming

- Increases branching
- Converts aliphatic hydrocarbons into aromatics (branched and aromatic hydrocarbons are better fuels for combustion engines).

Crude Oil

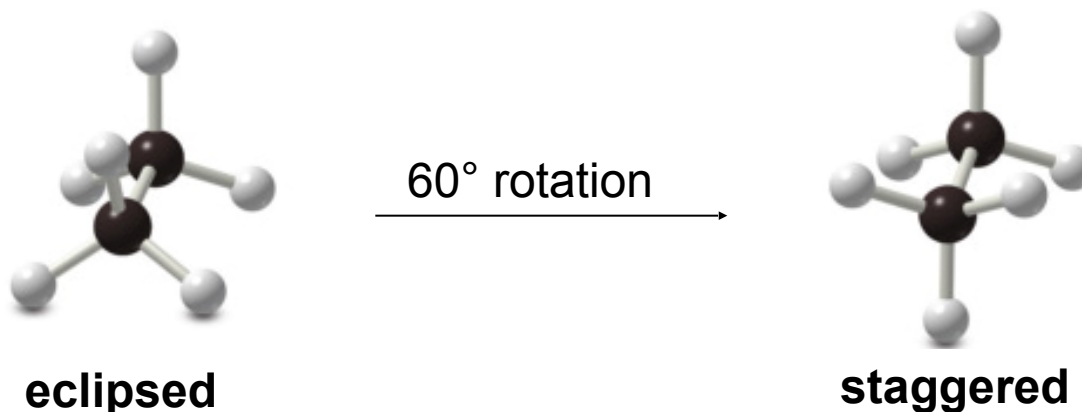


Barrel
42 gal
159 l

1 US gal = 3.78 l

Conformational Isomerism

Ethane



- ❑ In the **eclipsed** conformation, all C–H bonds are aligned.
- ❑ In the **staggered** conformation, C–H bonds on each carbon bisect the H–C–H angles on the other carbon.

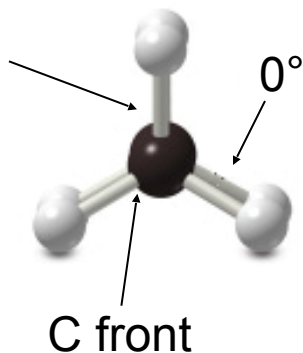
[modelli 3D](#)

Ethane Conformations

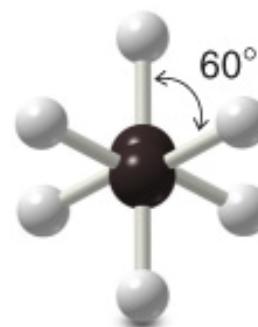
- ❑ The H-C-C-H angle is called dihedral angle (0° in the eclipsed and 60° in the staggered conformation).

View along the C-C bond

C back



60° rotation



Eclipsed conformation

Staggered conformation

The front C-H bonds bisect the H-C-H angles on the carbon atom at the back

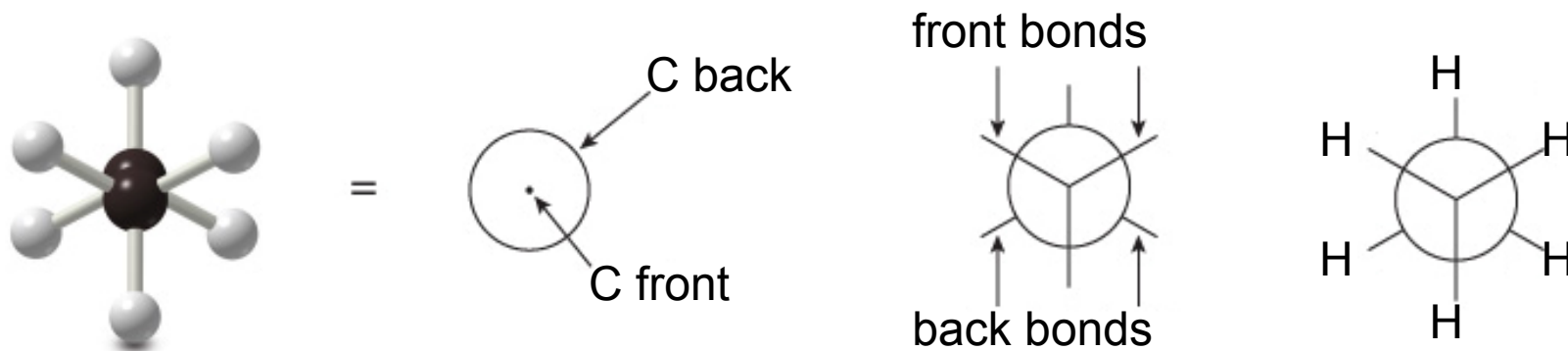
Newman Projection

□ How to draw a Newman projection

[1] Look along the C-C bond and draw a circle (the back C atom) with a dot in the centre (the front C atom).

[2] Draw the bonds

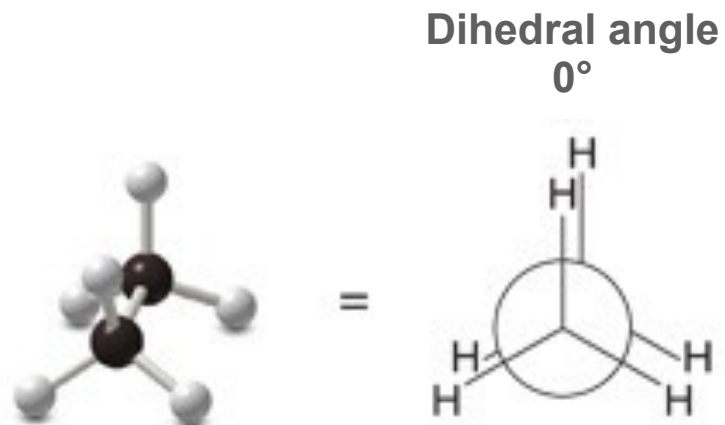
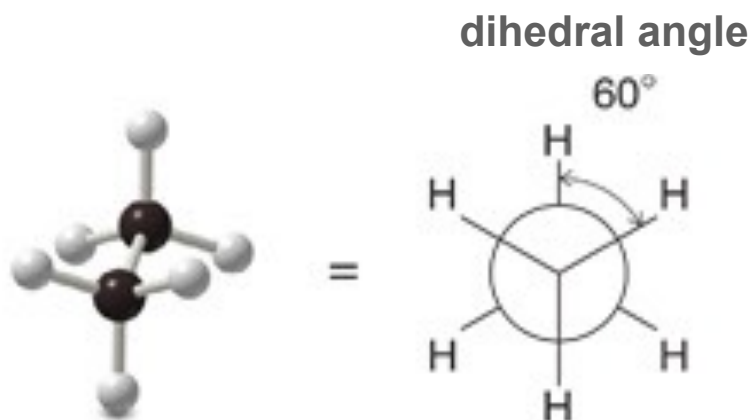
[3] Add the atoms



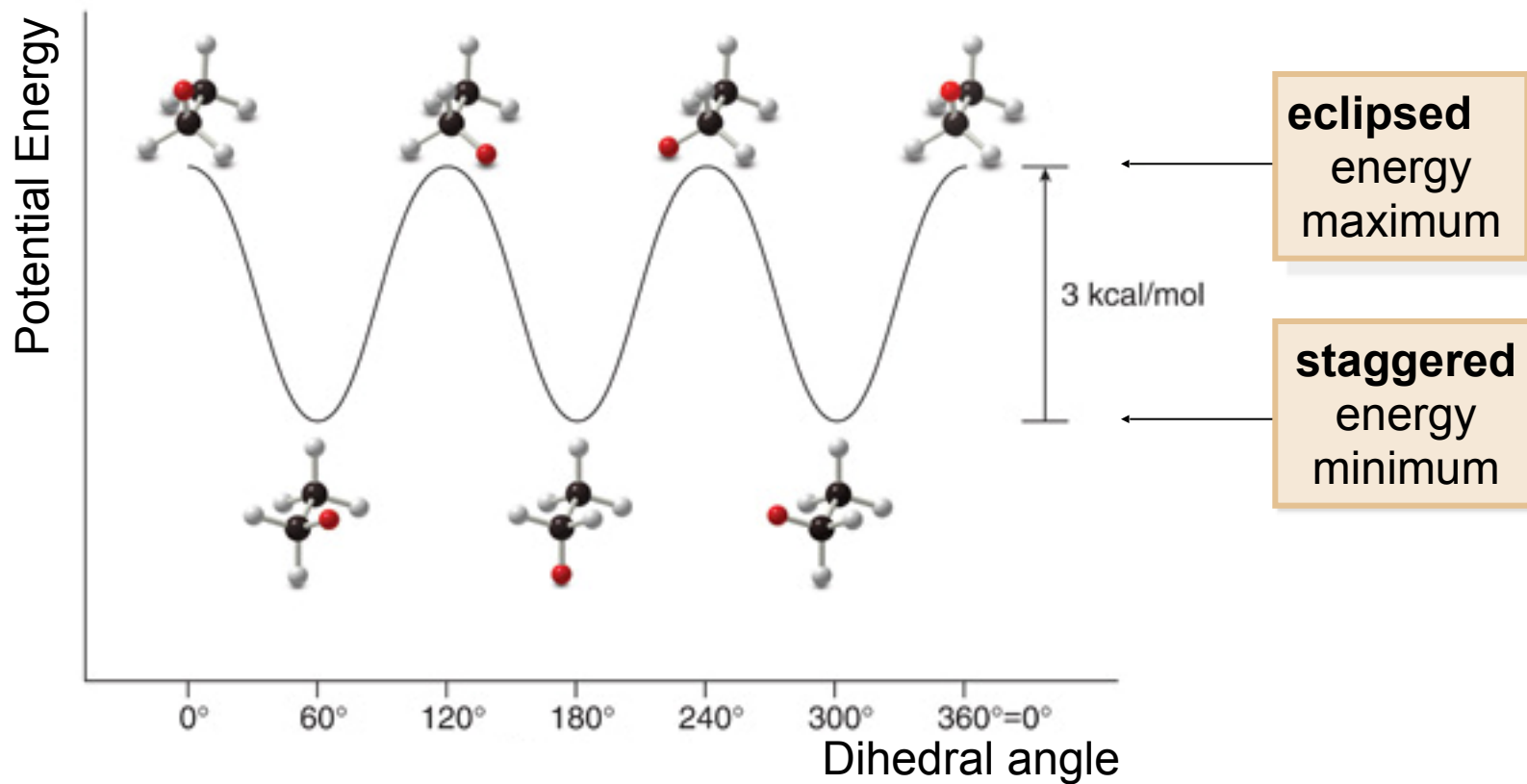
Newman Projections of Ethane

staggered conformation

eclipsed conformation

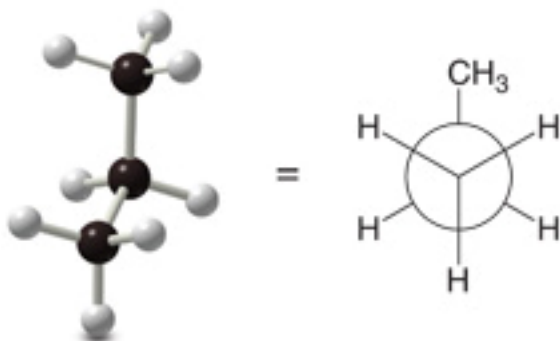
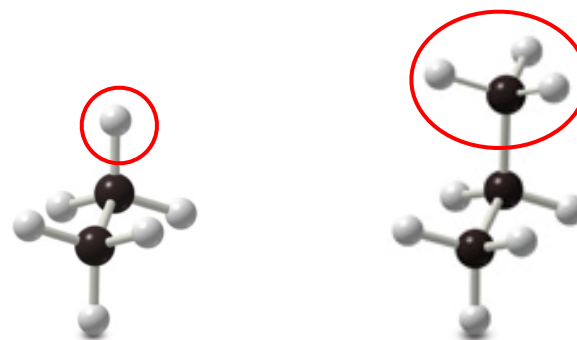
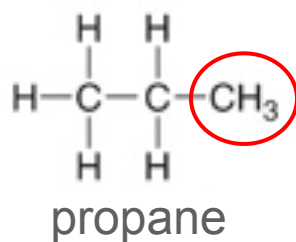
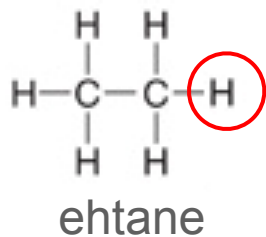


Conformations of Ethane

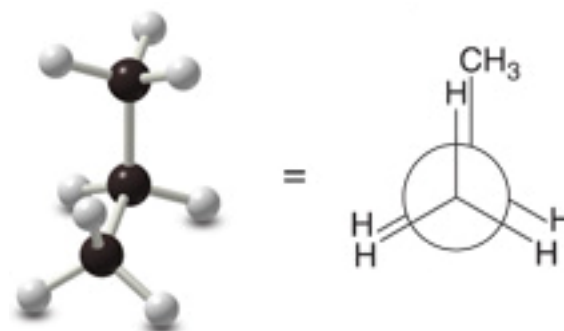


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[video](#)

Conformations of Propane

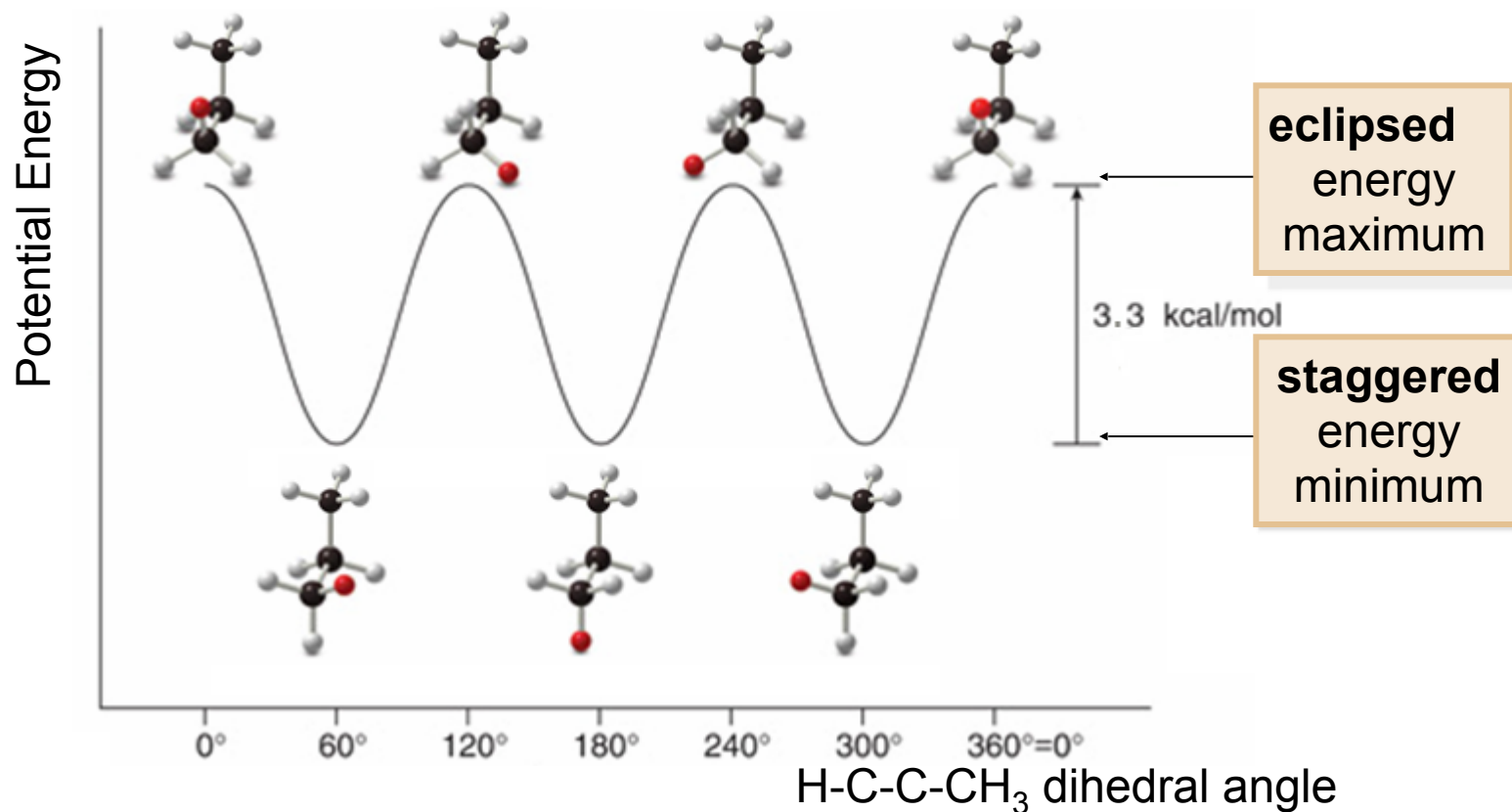


staggered conformation



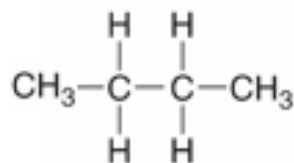
eclipsed conformation

Conformations of Propane

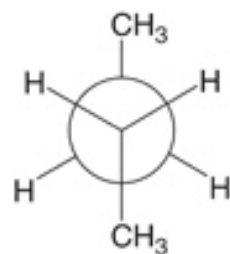


Torsional Strain (3.3 kcal/mole) is higher than in ethane. The methyl group is bulkier than a hydrogen atom

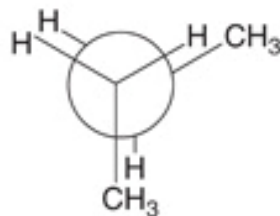
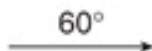
Conformations of Butane



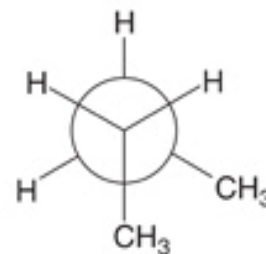
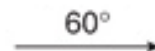
6 different conformations



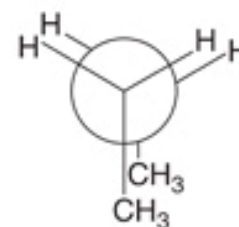
1
staggered, anti



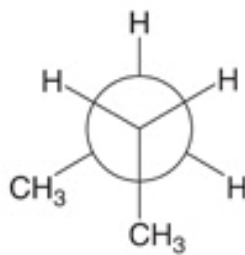
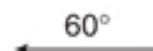
2
eclipsed



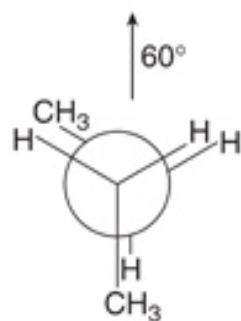
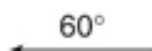
3
staggered, gauche



4
eclipsed



5
staggered, gauche



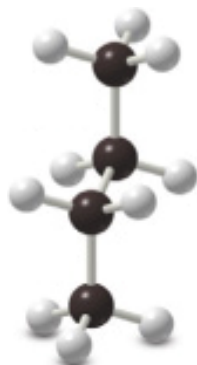
6
eclipsed



Conformations of Butane

A staggered conformation with two large groups at 180° is called *anti*

anti conformation



1

The CH_3 are at 180°

A staggered conformation with two large groups at 60° is called *gauche*.

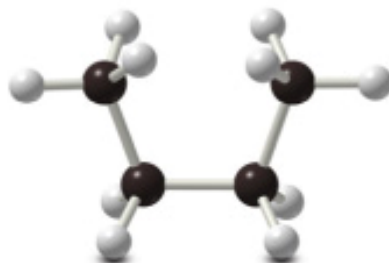
conformazione gauche



3

The CH_3 are at 60°
steric strain

Eclipsed conformation

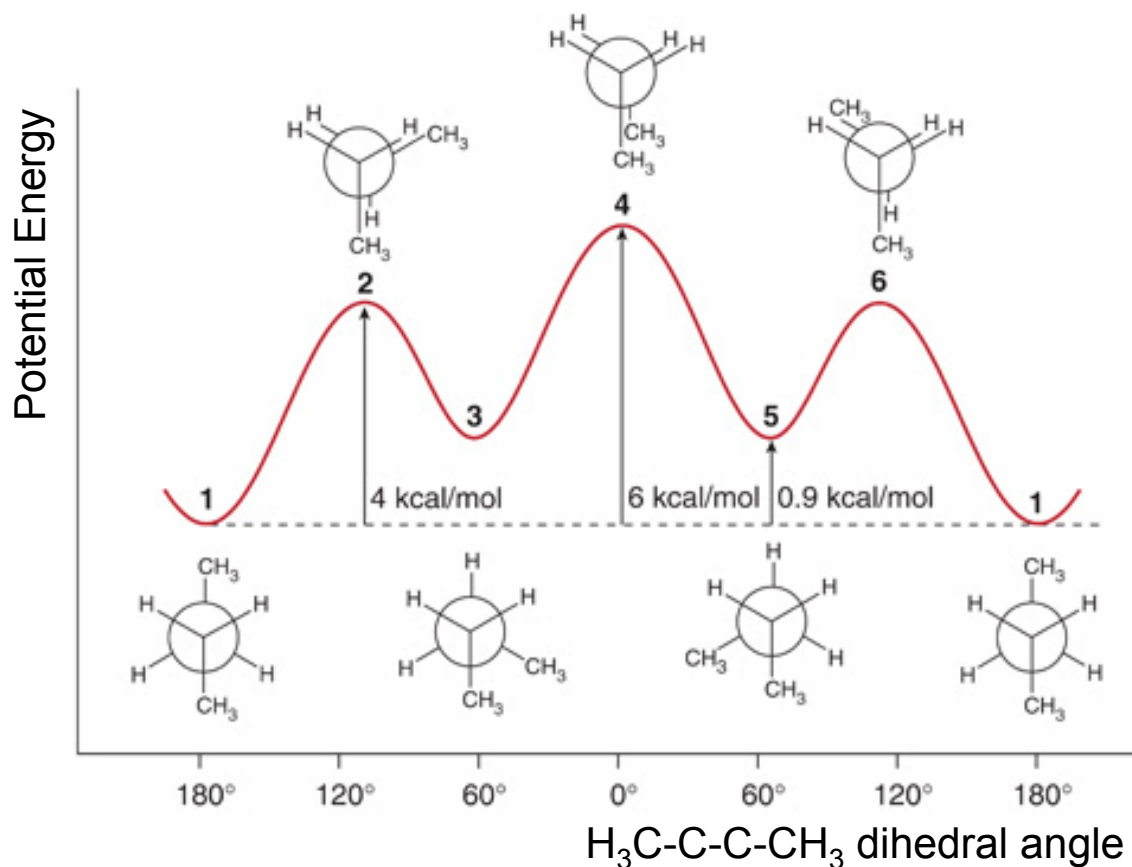


4

The CH_3 are at 0°
steric strain

Conformations of Butane

- *Staggered conformations:*
 - **1** (anti) is the absolute minimum
 - **3,5** (gauche) are relative minima
- *Eclipsed conformations:*
 - **4** is the absolute maximum (CH₃ eclipsed)
 - **2,6** are relative maxima

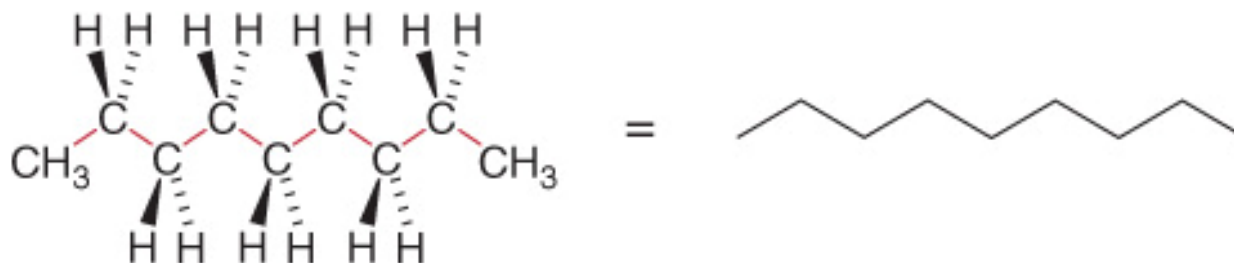


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[video](#)

Torsional Strain in Linear Alkanes

Interaction	Energy (kcal/mole)
Eclipsing H,H	1
Eclipsing H,CH ₃	1.5
Eclipsing CH ₃ ,CH ₃	4
Gauche CH ₃ ,CH ₃	0.9

- ❑ A **rotational barrier** is the energy difference between two minima.
- ❑ The most stable conformation of linear hydrocarbons is staggered with the bulky groups in anti. Thus long chains are usually drawn with a zigzag.



[modello 3D](#)

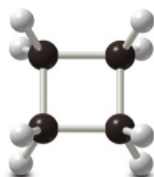
Cycloalkanes

Cycloalkanes

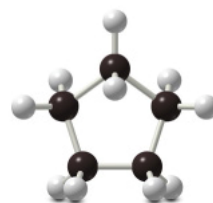
- Cycloalkanes have empirical formula C_nH_{2n} and contain carbon atoms arranged in a cyclic chain
- Nomenclature: cyclo + name of the corresponding alkane



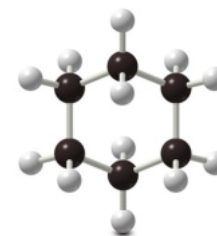
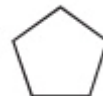
cyclopropane
 C_3H_6



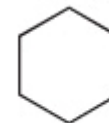
cyclobutane
 C_4H_8



cyclopentane
 C_5H_{10}



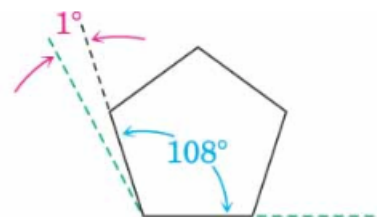
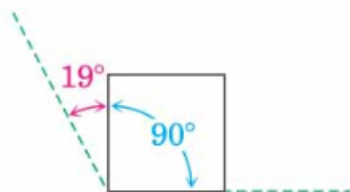
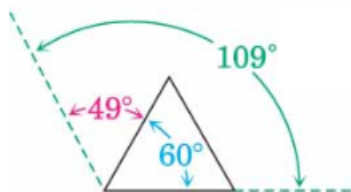
cyclohexane
 C_6H_{12}



[modelli 3D](#)

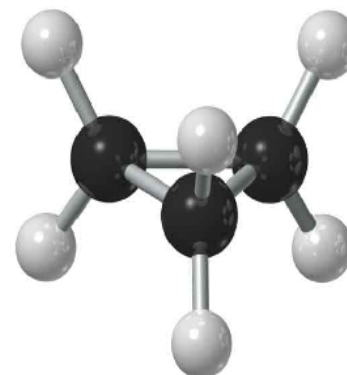
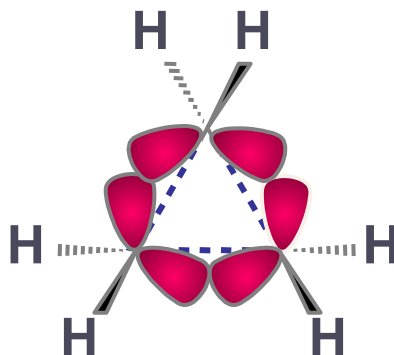
Stability: Angular Strain (Baeyer's Strain)

- ❑ Baeyer (1885): as carbon prefers 109° bond angles, rings other than five or six membered may be too **strained** to exist.
- ❑ Cycloalkanes from C_3 to C_{30} do exist, but some of them are strained because of distorted bond angles and other interactions.



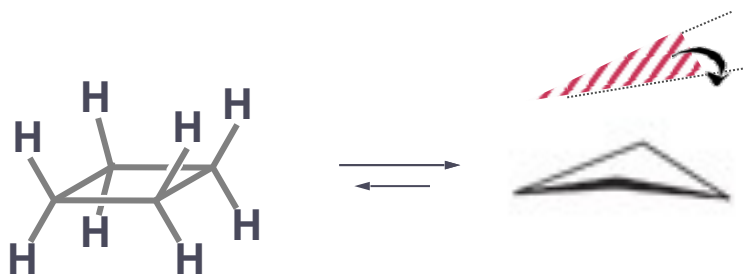
Cyclopropane C₃H₆

- ❑ Planar.
- ❑ Angle strain: 60° CCC angles.
- ❑ Torsional strain: all H are eclipsed.
- ❑ May be described as sp³ hybridized with banana bonds.



Cyclobutane C₄H₈

- ❑ In planar cyclobutane all hydrogens would be eclipsed.
- ❑ To relieve torsional strain, cyclobutane is puckered by about 25°.
- ❑ In doing so the CCC bond angles decrease to 88° and hydrogens on opposite carbons become closer.



25°
puckering
angle



Planar
angle strain
torsional strain

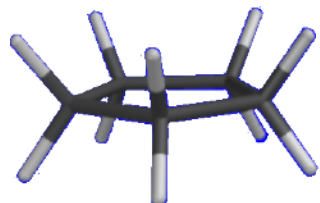
Puckered
slightly higher angle strain
lower torsional strain
some VdW strain

Ring Strain

Stability of cycloalkanes depend on **ring strain**:

- **angle strain**: distorted bond angles.
- **torsional strain**: eclipsing of C-H bonds.
- **VdW or steric strain**: repulsions between non bonded atoms.

Cyclopentane C₅H₁₀

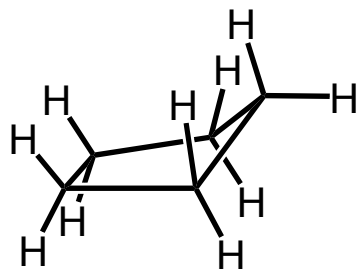
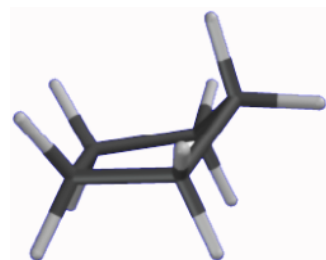


angle strain
torsional strain

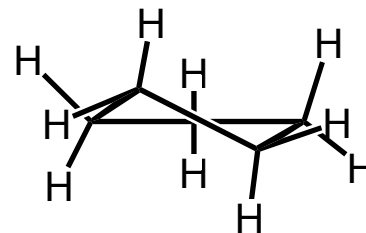


25°
puckering angle

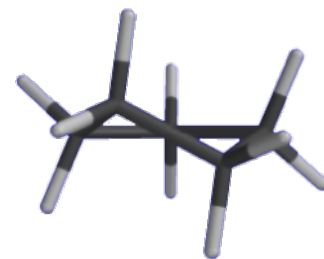
“envelope” conformation
eclipsing is partially relieved



envelope



half-chair

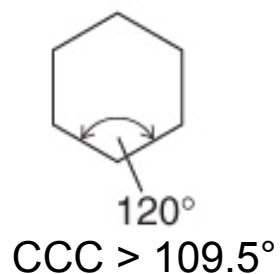


envelope and *half-chair* conformations have similar energies and rapidly interconvert into one another

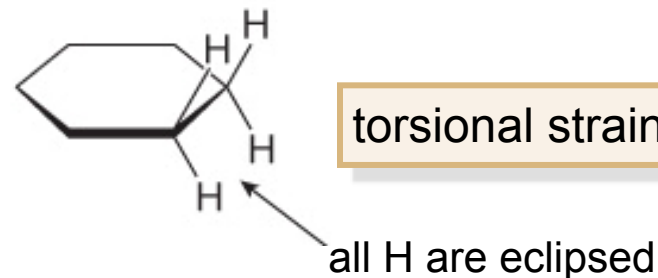
Cyclohexane C₆H₁₂

❑ Planar cyclohexane.

angle strain

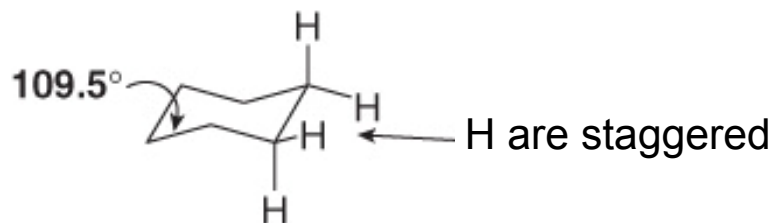


torsional strain

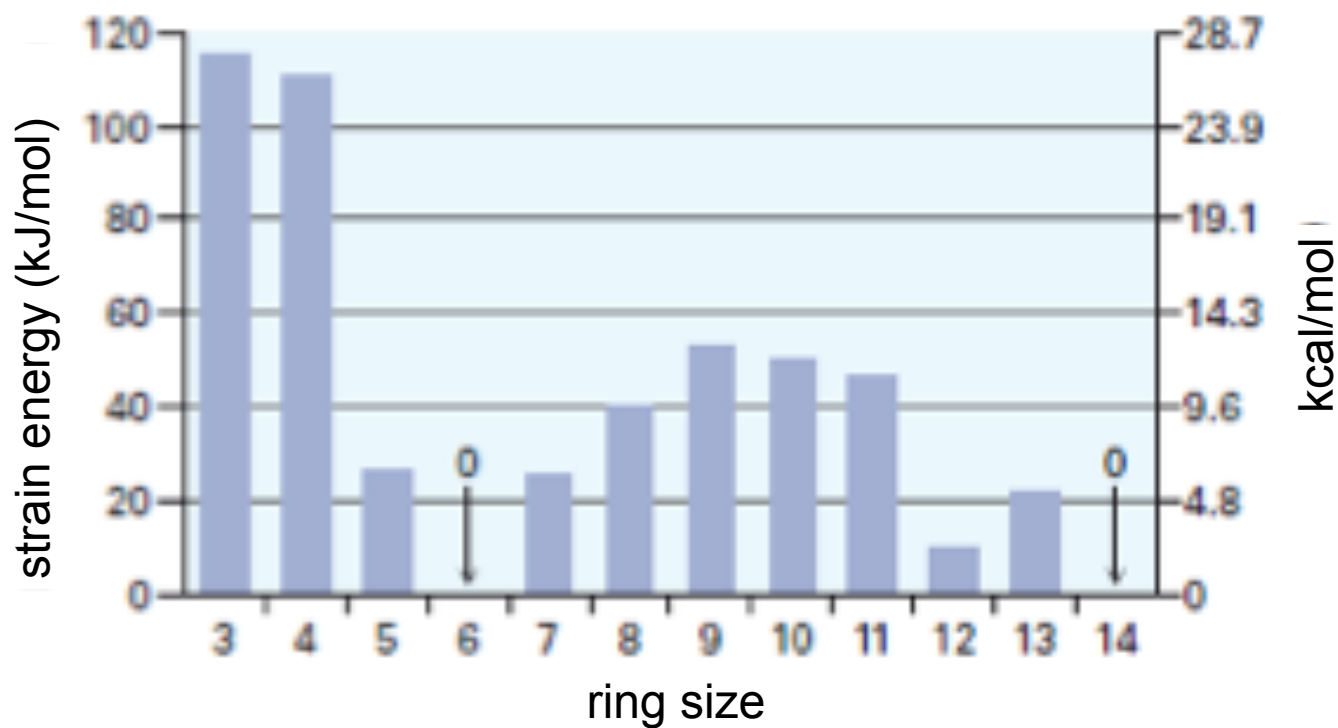


❑ *Chair* conformation.

strainless

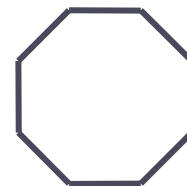
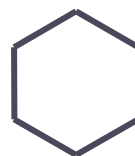





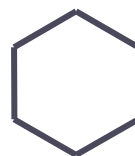

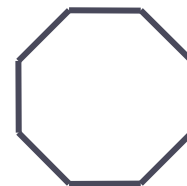
Strain Energies of Cycloalkanes



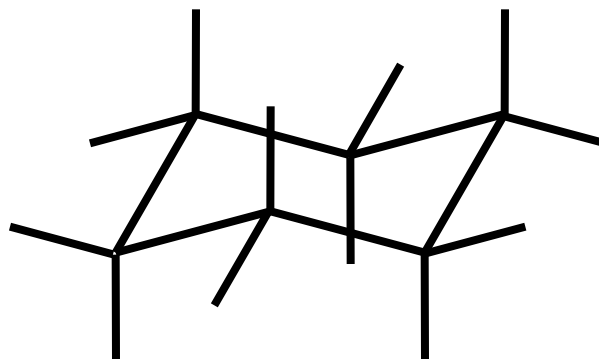
Strain Energies of Cycloalkanes

- Heats of combustion are used to calculate strain energies of cycloalkanes.
- Heats of combustion increase with the number of C atoms.
- Cyclohexane is taken as reference (Strain = 0).



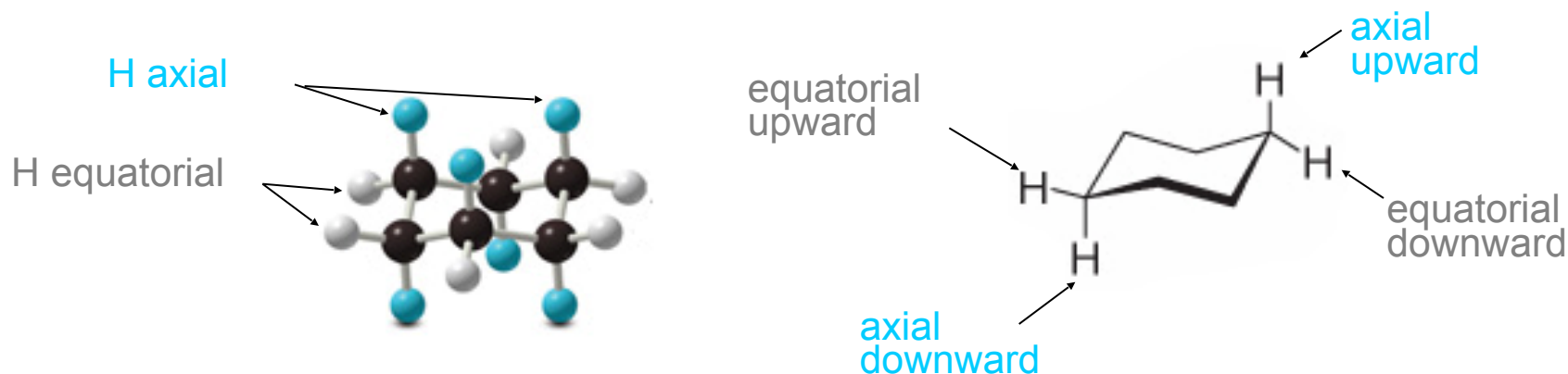
						
kJ/mol	2091	2724	3290	3910	4599	5264
Per CH ₂	697	681	658	653	657	658
Strain	132	112	25	0	28	40

How to Draw Chair Cyclohexane



Chair Conformation of Cyclohexane

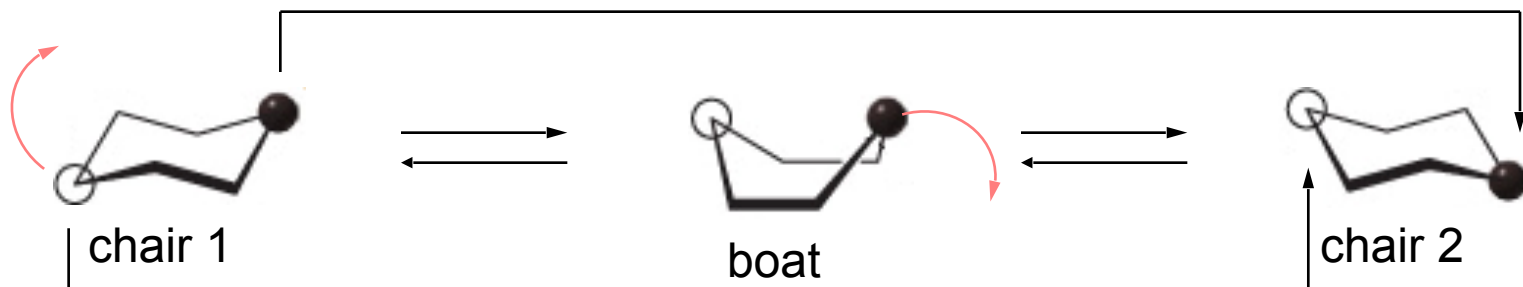
- ❑ There are two types of hydrogens:
 - **Axial**: perpendicular to the ring's mid-plane, above and below the ring.
 - **Equatorial**: in the ring's mid-plane, all around the ring.



- ❑ There are 6 axial and 6 equatorial hydrogens in cyclohexane.

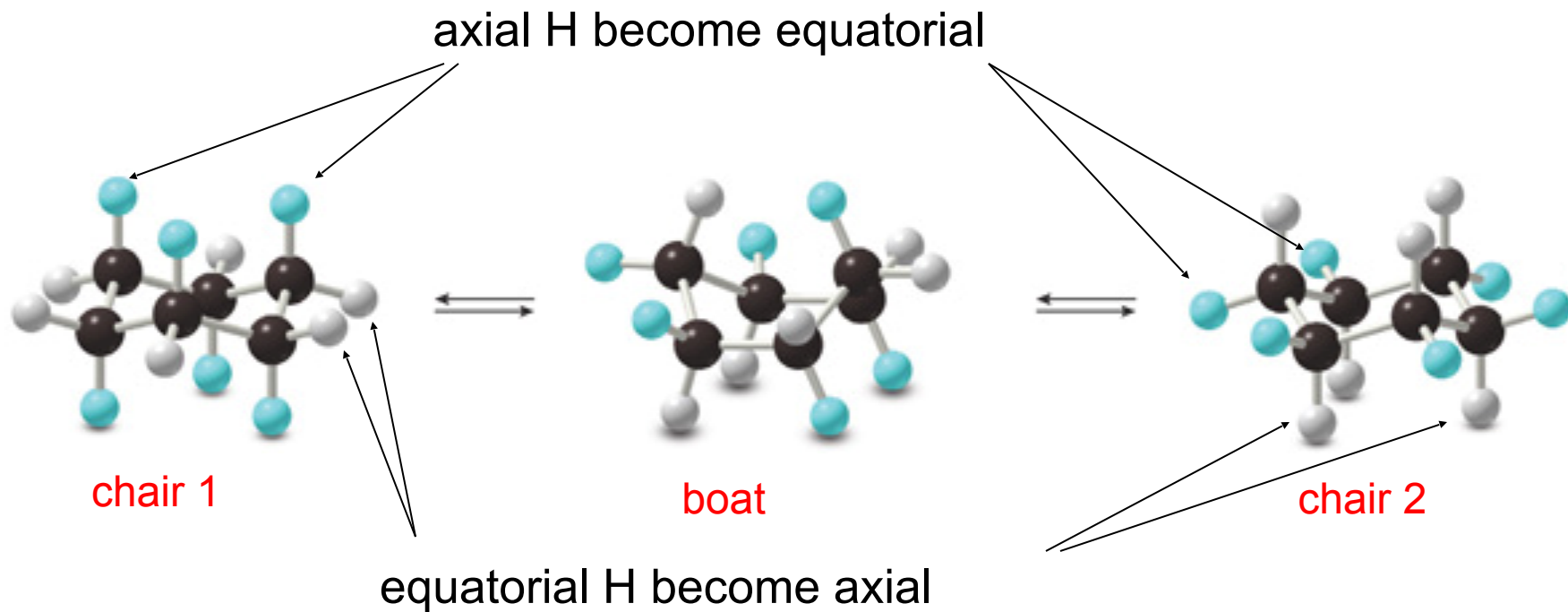
Ring Flipping

- ❑ **Ring flipping** is the interconversion between two chair conformations of cyclohexane.
- ❑ Upwards C become downwards and viceversa.
- ❑ Axial H become equatorial and viceversa.



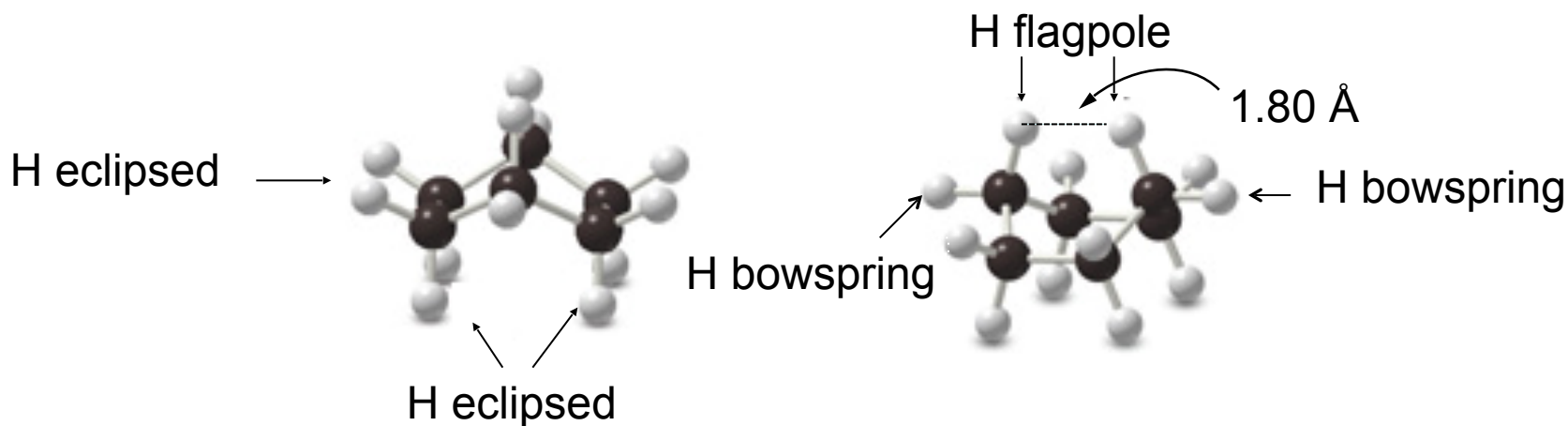
[video](#)

Ring Flipping

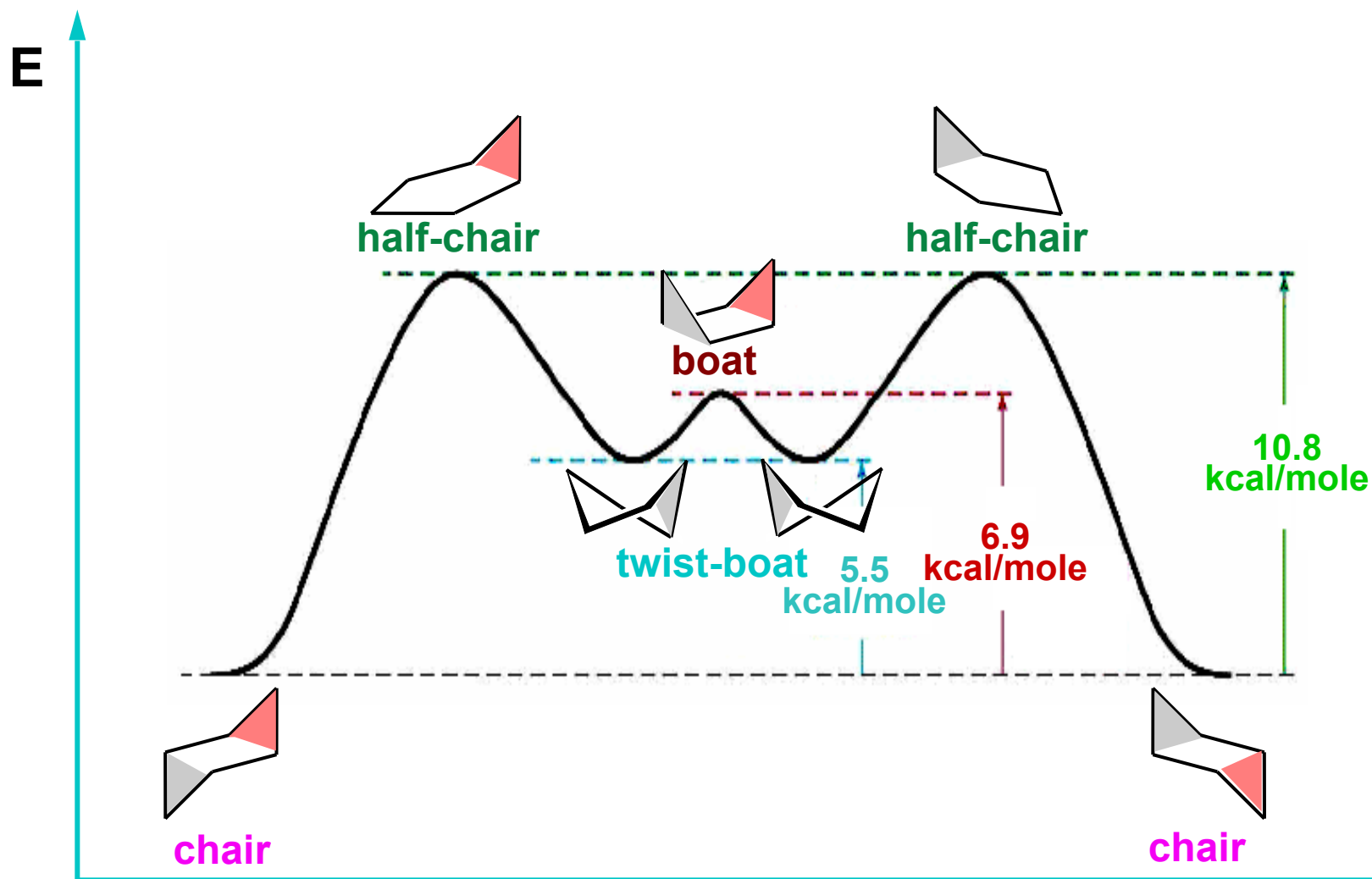


Conformations of Cyclohexane

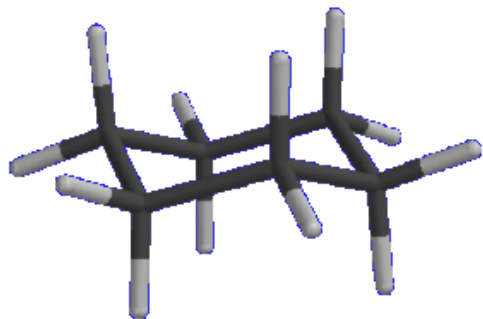
- ❑ Chair conformations are 7 kcal/mol more stable than boat conformations.
- ❑ **Torsional strain.** In the boat conformation the H on the base are eclipsed.
- ❑ **Steric strain.** Flag pole H are forced in close proximity.



Conformations of Cyclohexane

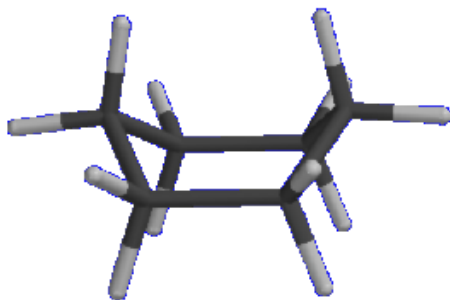


Conformations of Cyclohexane



chair

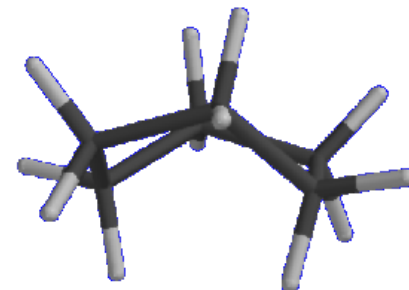
no ring strain
(99.99% at 25°C)



boat

- torsional strain
- steric strain

ring strain: ~ 7 kcal

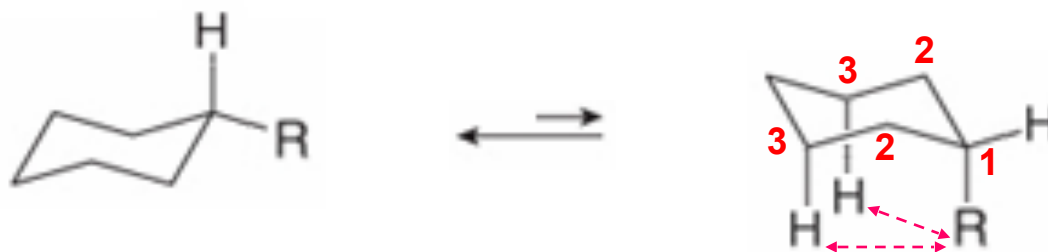


twist-boat

~ 1.5 kcal more stable
than the boat
(0.01% at 25°C)

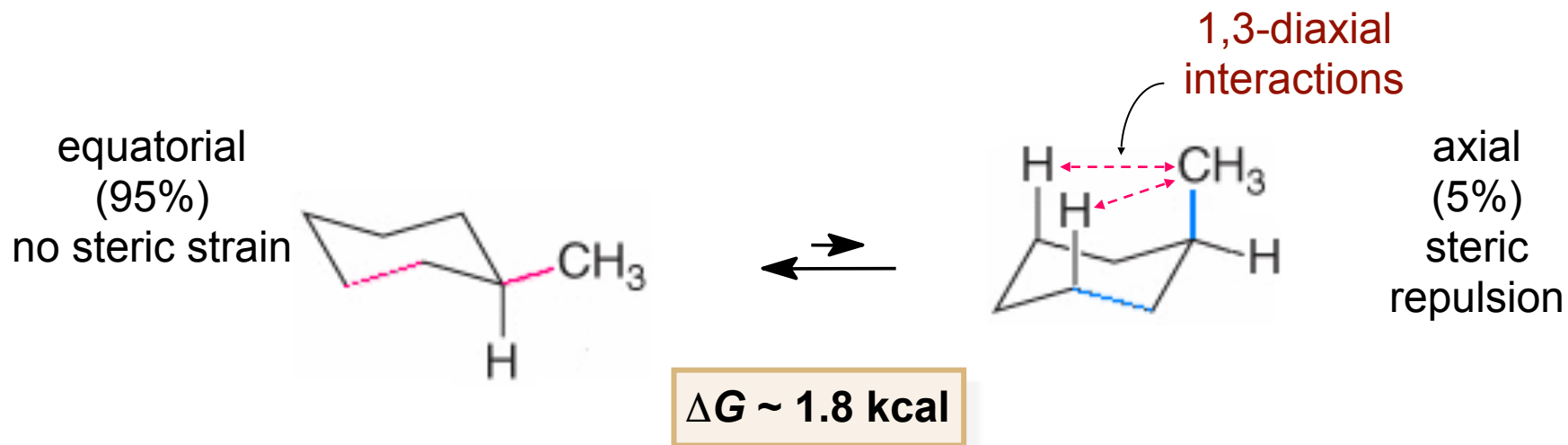
Substituted Cyclohexanes

- ❑ The chair conformations are no longer equivalent: they have different energies.



- ❑ The axial conformer is destabilized by **1,3-diaxial interactions** (VdW interactions) between the substituent and axial hydrogens.
- ❑ The larger the substituent, the less stable the axial conformation.

Methylcyclohexane

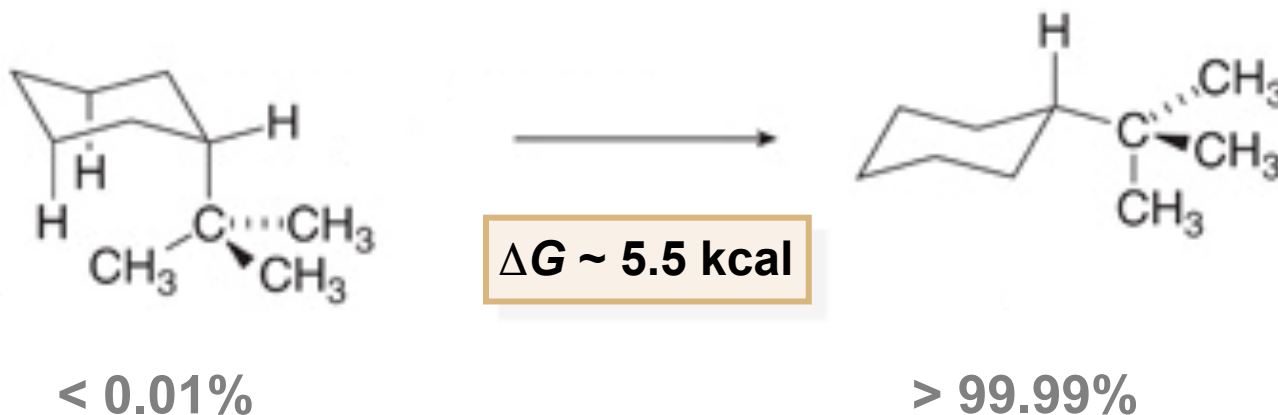


Each CH_3 / H interaction destabilizes the axial conformer by 0.9 kcal/mol

[modelli](#)

tert-Butylcyclohexane

- ❑ The *tert*-butyl group is so bulky that there is no axial conformer at the equilibrium.



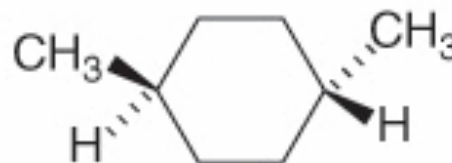
The *tert*-butyl group **freezes** the conformational equilibrium.

Disubstituted Cyclohexanes. Geometrical Stereoisomerism

- There are two isomers of 1,4-dimethylcyclohexane.



cis

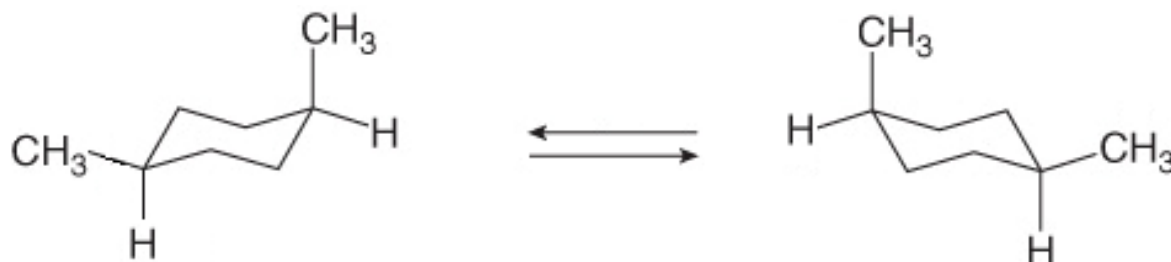


trans

- Each geometrical isomer has two possible chair conformations.

1,4-Dimethylcyclohexane

cis



$$\Delta G = 0 \text{ kcal}$$

equatorial-axial
2 1,3-diaxial interactions
 $2 \times 0.9 = 1.8 \text{ kcal}$

axial-equatorial
2 1,3-diaxial interactions
 $2 \times 0.9 = 1.8 \text{ kcal}$

trans



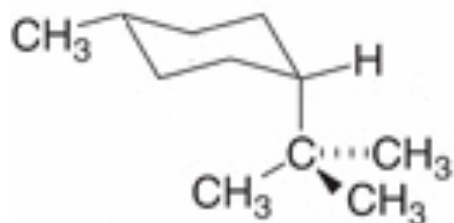
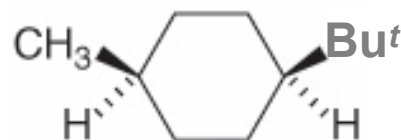
$$\Delta G \sim 3.6 \text{ kcal}$$

bisaxial
4 1,3-diaxial interactions
 $4 \times 0.9 = 3.6 \text{ kcal}$

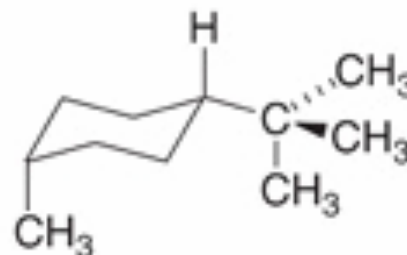
bisequatorial
no repulsions

cis-1-t-Butyl-4-methylcyclohexane

- ❑ The conformational equilibrium is frozen by the bulky t-butyl group.



5.5 kcal/mol

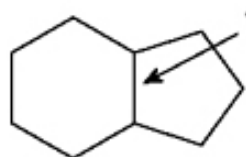


1.8 kcal/mole

$\Delta G \sim 3.7$ kcal

Polycyclic compounds

A fused bicyclic system



This C—C bond is **shared** by both rings.

- One bond is shared by two rings.
- The shared C's are adjacent.

A bridged bicyclic system



These C's are **shared** by two rings.

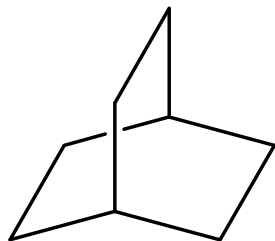
- Two non-adjacent atoms are shared by both rings.

A spiro bicyclic system

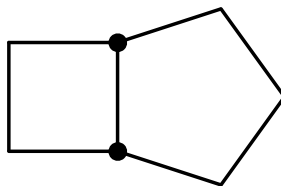


- One atom is shared by two rings

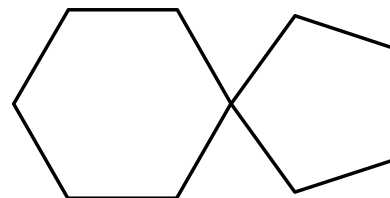
Polycyclic compounds



bicyclo[2.2.2]octane



bicyclo[3.2.0]heptane

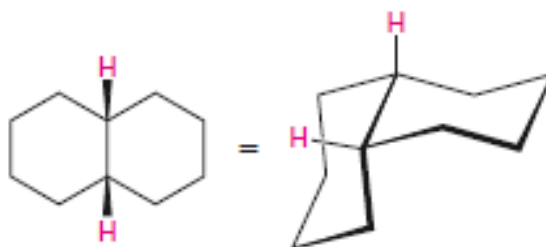


spiro[4,5]decane

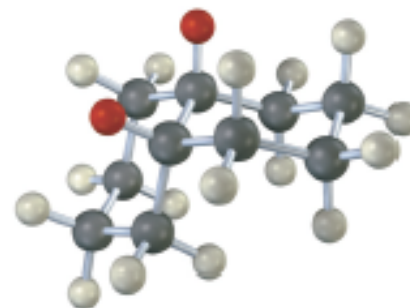
[modelli](#)

Polycyclic Hydrocarbons

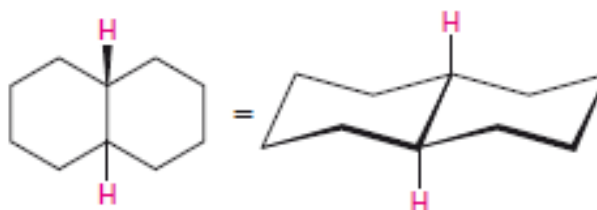
less stable
(1 axial substituent)



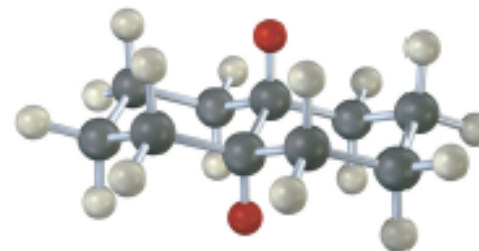
cis-decaline



more stable
(equatorial substituents)

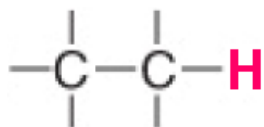


trans-decaline

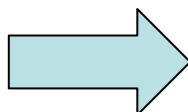


[modelli](#)

Reactions of Alkanes



- no lone pairs
- no π bonds
- no heteroatoms
- not nucleophilic
- not electrophilic
- strong, not polar C–C, C–H bonds



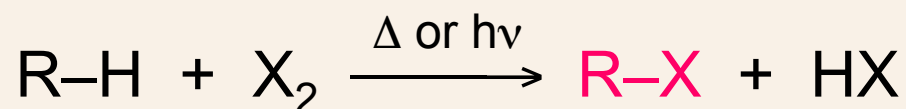
Alkanes react only at high temperatures, with radical mechanisms.

Halogenation of Alkanes

**Chapt. 10 Organic Chemistry, 8th Edition
John E. McMurry**

Halogenation of Alkanes

- ❑ In the presence of heat or light, alkanes react with halogens, with a radical mechanism, to give alkyl halides.



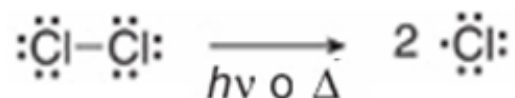
radical substitution

- ❑ Halogenation of alkanes is carried out with Cl_2 or Br_2 . The reaction with F_2 is too violent and the reaction with I_2 is too slow.

Halogenation of Methane

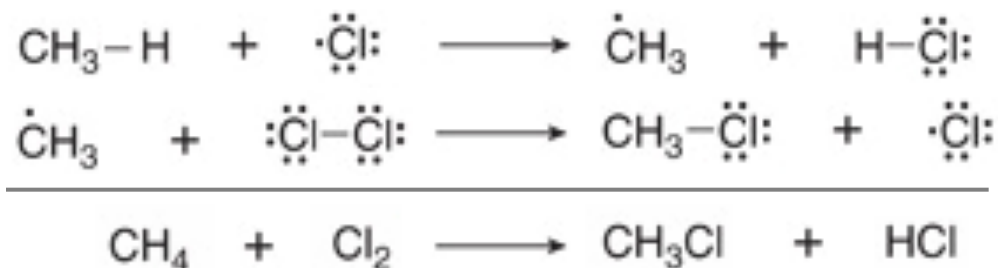
Initiation

Stage [1]: formation of $\text{Cl}\cdot$ radicals



Propagation

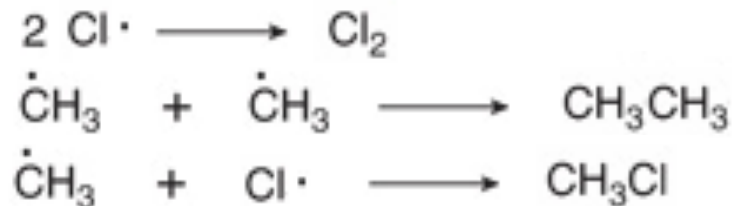
Stages [2] and [3]: A new radical is formed for each reacting radical



thousands of
cycles.
Chain reaction

Termination

Stage [4]: Two radicals recombine forming a σ bond.



[video](#)

Energetics

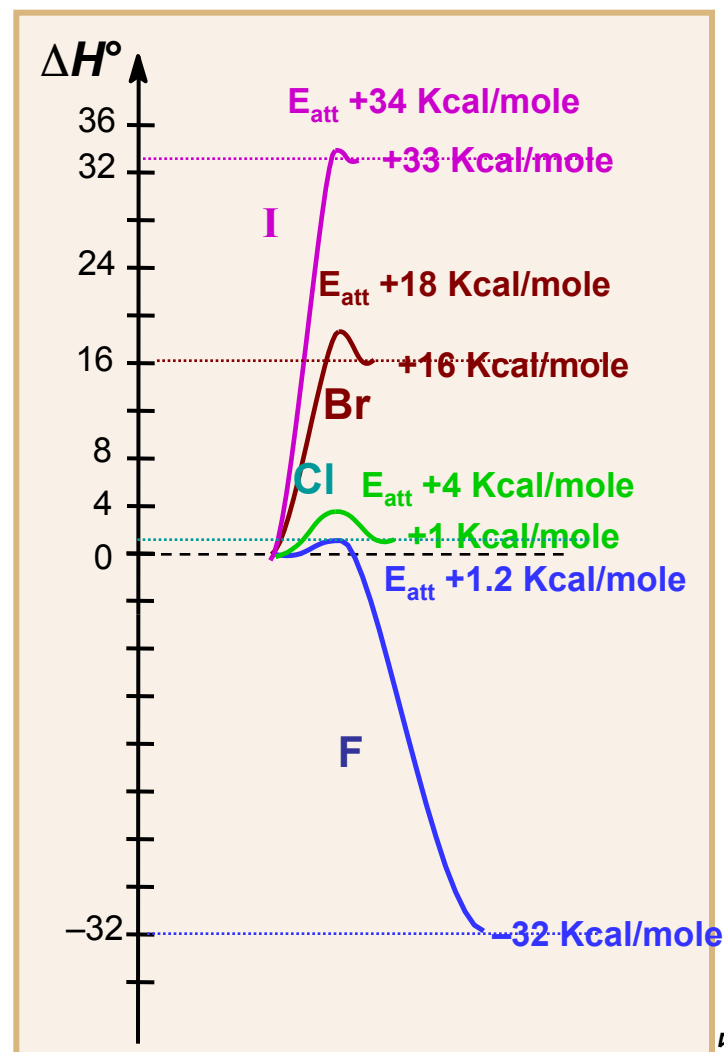
Stage [2] is the slow step:



$$\Delta H^\circ = \Delta H^\circ(\text{C-H}) - \Delta H^\circ(\text{X-H})$$

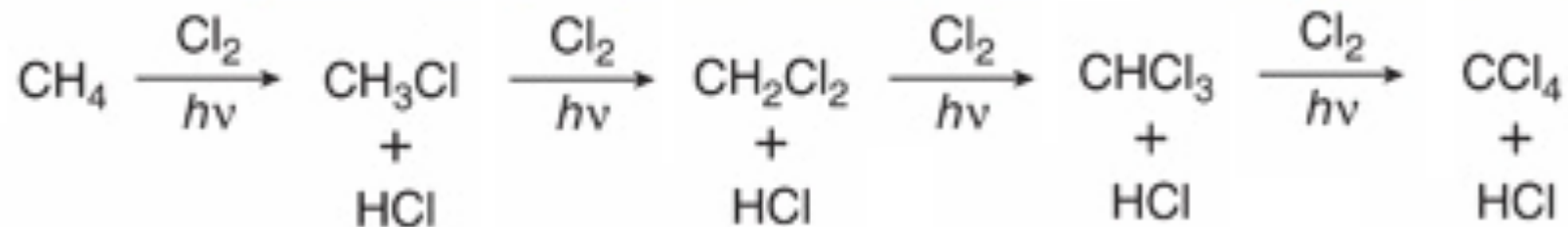
ΔH° , Kcal/mole

$\Delta H^\circ(\text{C-H})$	104			
X =	F	Cl	Br	I
$\Delta H^\circ(\text{X-H})$	136	103	88	71
ΔH°	-32	+1	+16	+33



Halogenation of Alkanes

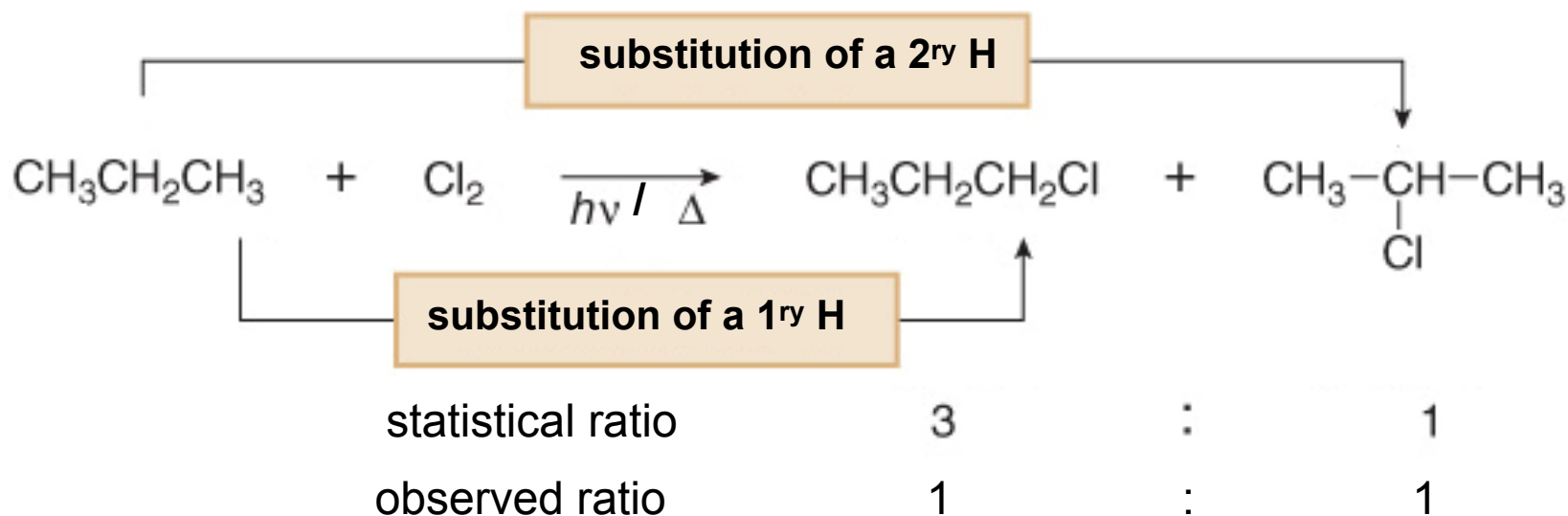
- Monohalogenation is only possible with an excess of substrate, otherwise polyhalogenation predominates.



- Problem: mixture of halogenated products.
- Solution: CH_4 in large excess and recycled.

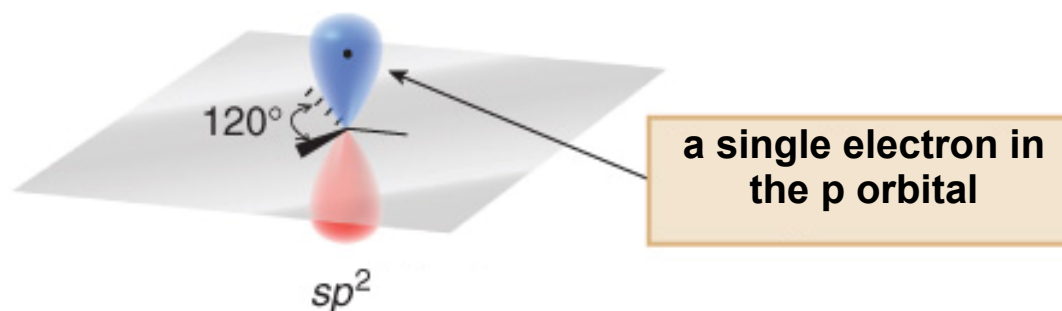
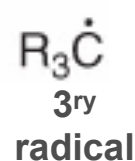
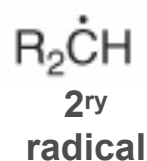
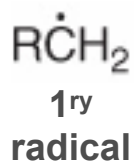
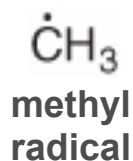
Regioselectivity

- Isomers are formed in the halogenation of propane and higher hydrocarbons:



Structure of Radicals

- ❑ Alkyl radicals are sp^2 hybridized with a trigonal planar geometry.
- ❑ The p orbital contains an unpaired electron.



C-H Bond Dissociation Energies

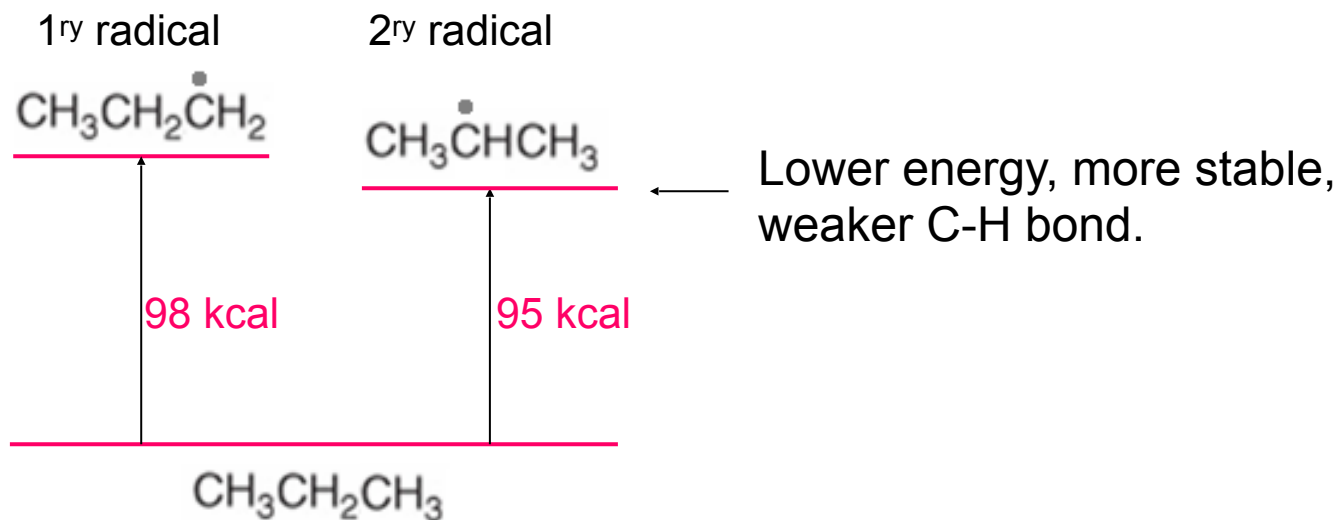


DH = BDE bond dissociation energy

$\text{CH}_3\text{-H}$	104 kcal/mole		$\dot{\text{C}}\text{H}_3$	methyl radical
$\text{CH}_3\text{CH}_2\text{-H}$	98 kcal/mole		$\text{R}\dot{\text{C}}\text{H}_2$	1 ^{ry} radical
$\text{CH}_3\text{CH}_2\text{CH}_2\text{-H}$	98 kcal/mole	(1 ^{ry} C-H)		
$\text{CH}_3\text{CH}(\text{H})\text{CH}_3$	95 kcal/mole	(2 ^{ry} C-H)	$\text{R}_2\dot{\text{C}}\text{H}$	2 ^{ry} radical
$\text{CH}_3\text{C}(\text{CH}_3)_2\text{-H}$	91 kcal/mole	(3 ^{ry} C-H)	$\text{R}_3\dot{\text{C}}$	3 ^{ry} radical

Reactivity of C-H bonds:
 $3^{\text{ry}} > 2^{\text{ry}} > 1^{\text{ry}} > \text{CH}_3\text{-H}$

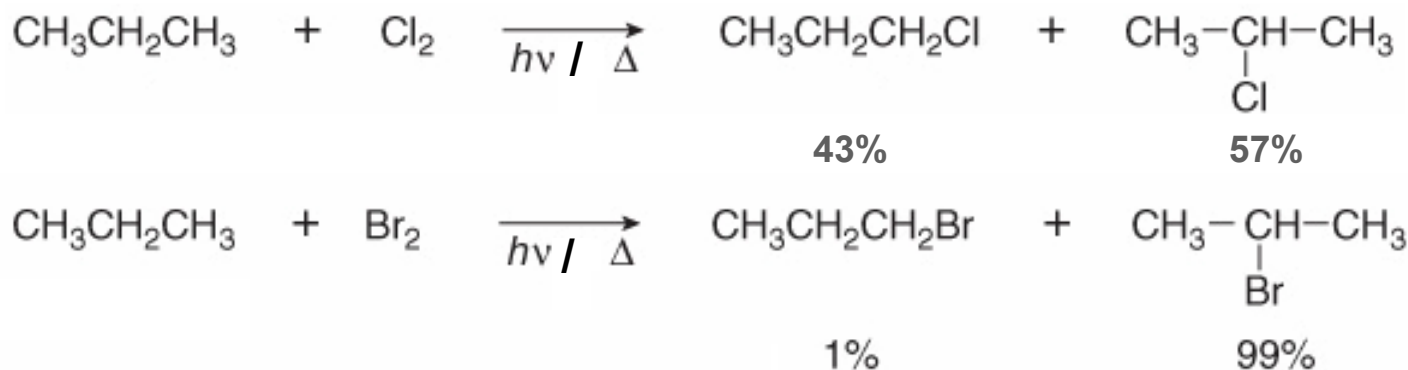
Regioselectivity



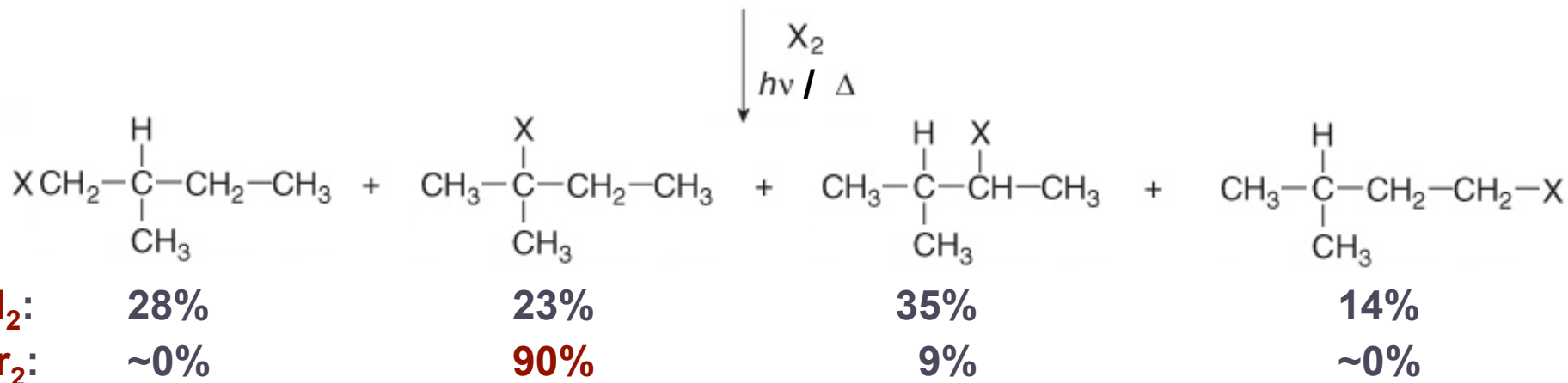
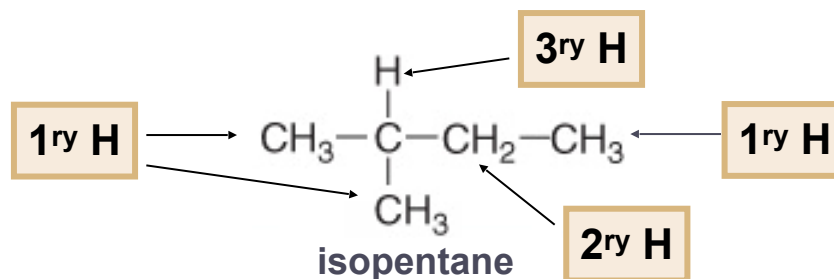
- ❑ Radical stability: $3^{\text{ry}} > 2^{\text{ry}} > 1^{\text{ry}}$.
- ❑ Strength of C-H bonds: $3^{\text{ry}} < 2^{\text{ry}} < 1^{\text{ry}}$.

Reactivity and Selectivity

- Chlorination of alkanes is faster than bromination.
- Bromination of alkanes is more selective.



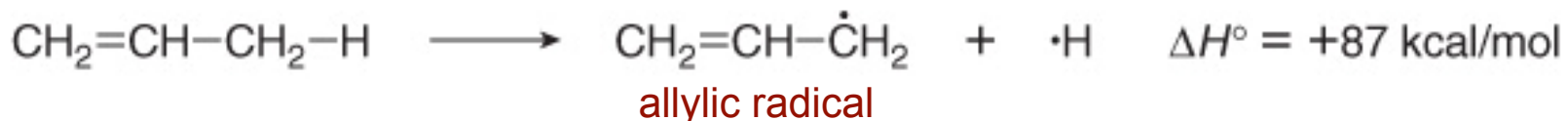
Regioselectivity



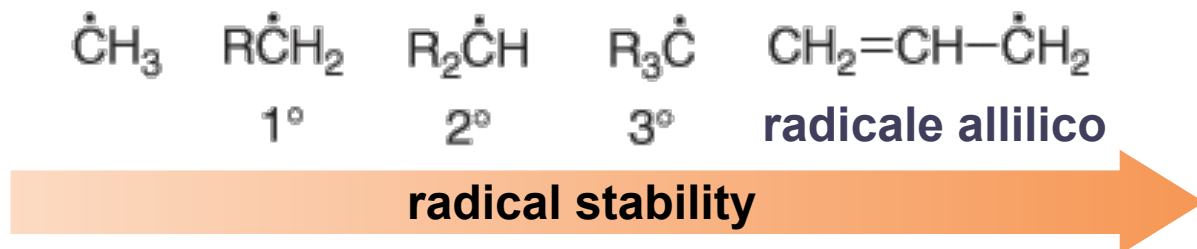
C-H relative reactivity	3ry	2ry	1ry
with Cl₂	5.2	3.9	1
with Br₂	1640	82	1

Halogenation of Allylic Carbons

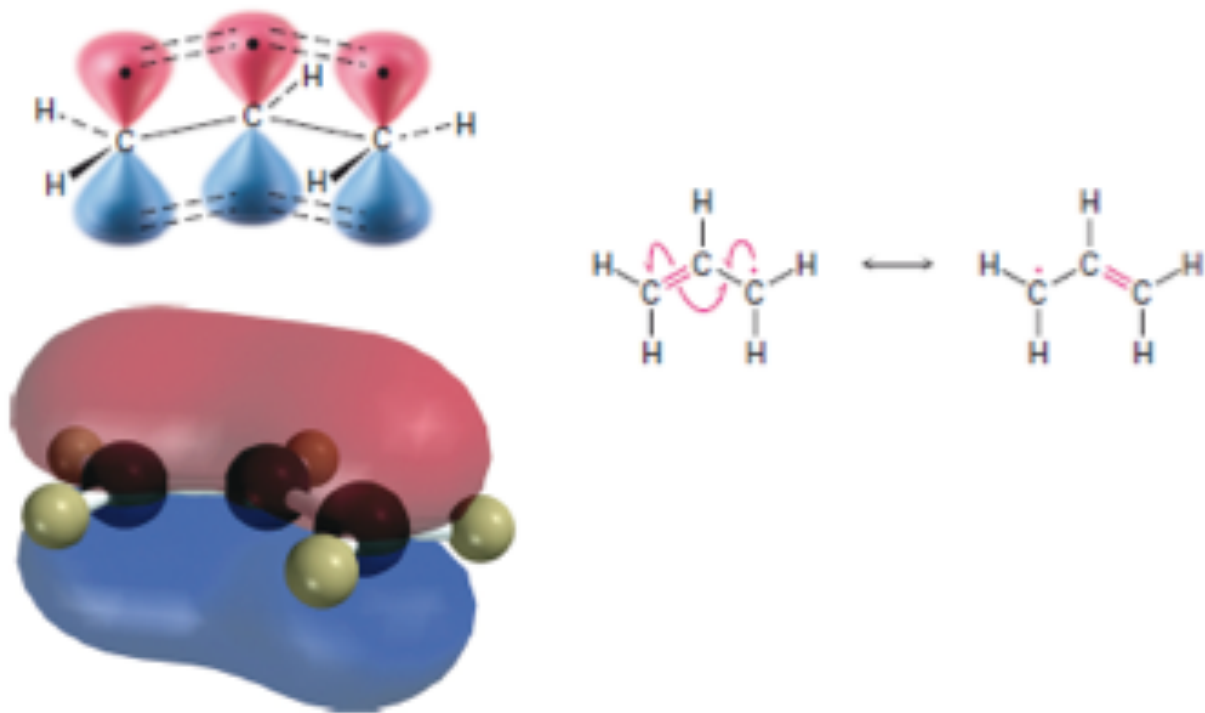
- Allylic carbons are sp^3 carbons adjacent to a double bond.
- A resonance-stabilized **allylic radical** is obtained by homolysis of an allylic C–H bond.



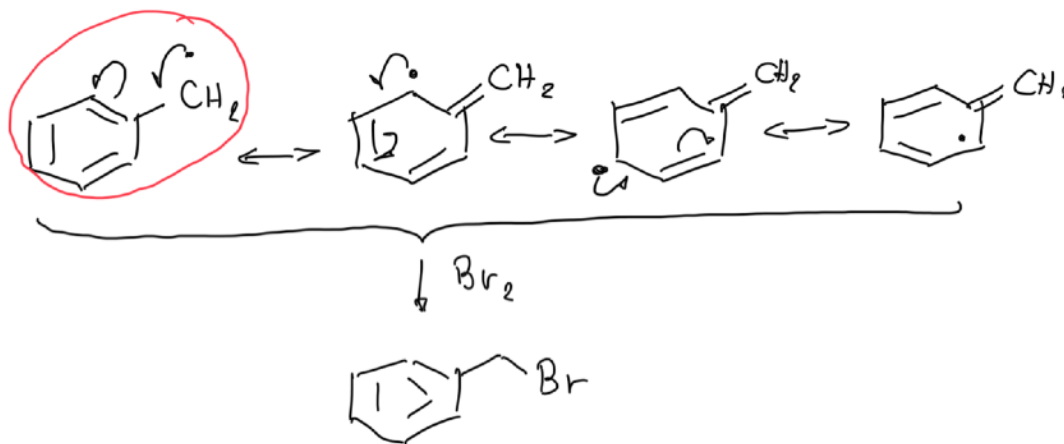
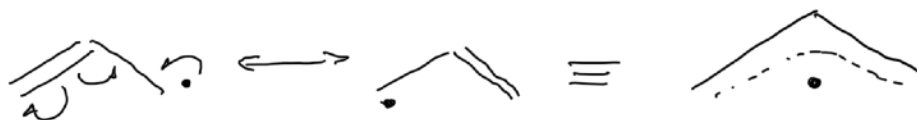
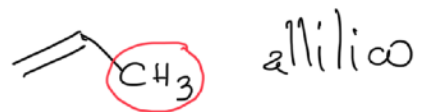
- BDEs of allylic C–H bonds are approximately 4 kcal/mol lower than BDE for 3^o C–H bonds.
- The delocalized allylic radical is more stable than a 3^o radical.



The Allylic Radical

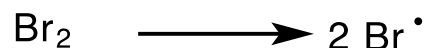


Delocalized Radicals

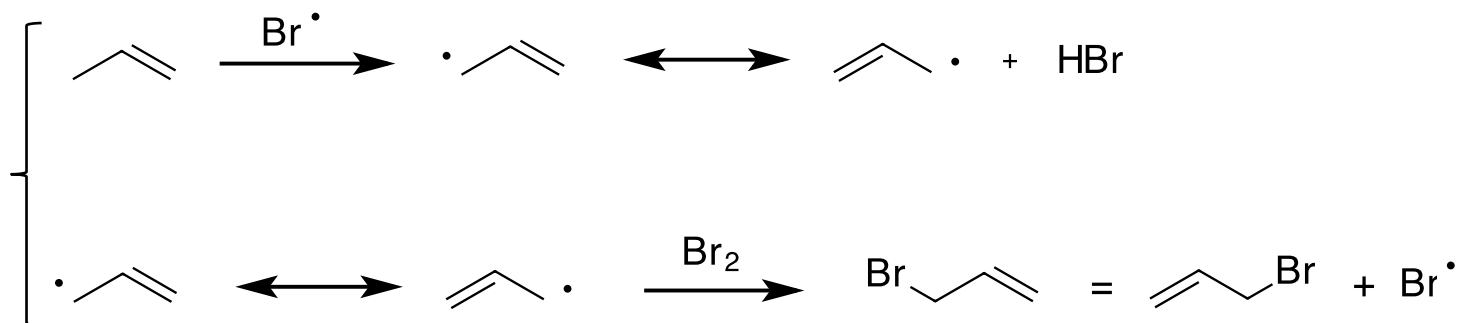


Halogenation of Allylic Carbons

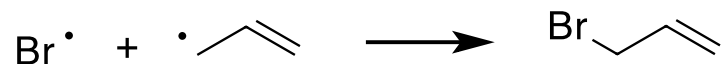
initiation



propagation

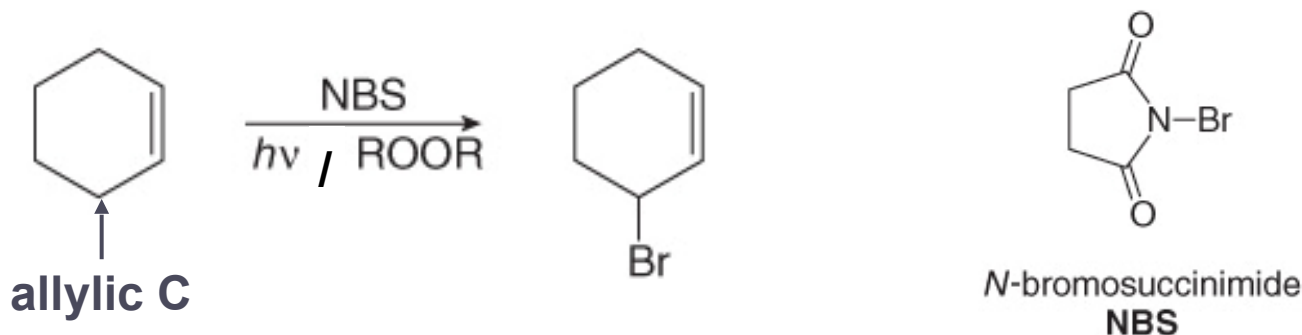


termination

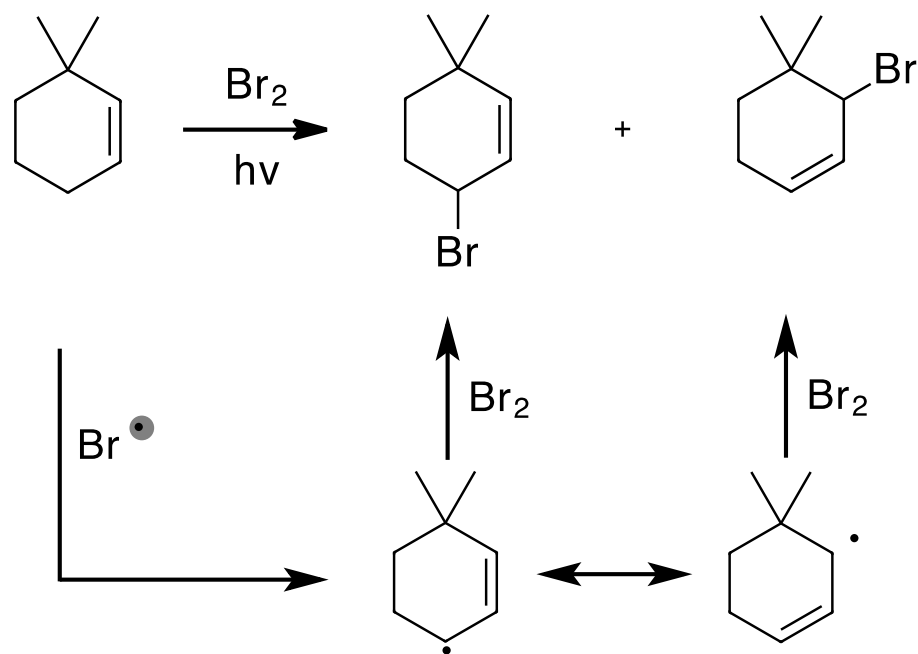


Halogenation of Allylic Carbons

- ❑ Allylic carbons can be selectively brominated with NBS and UV irradiation or a radical initiator.
- ❑ Breaking of the weak N-Br bond of NBS initiates the radical chain reaction.

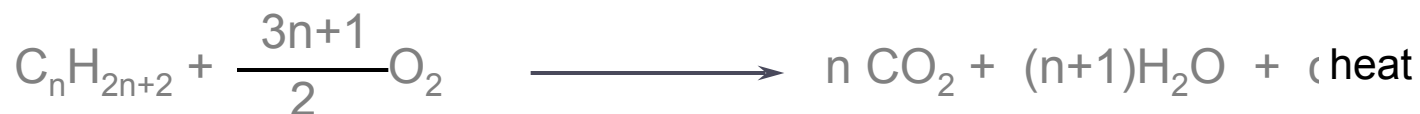
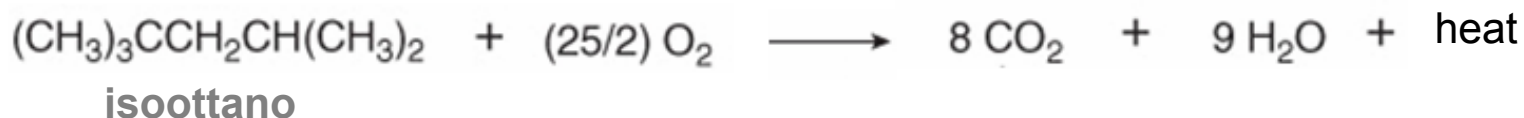


Halogenation of Allylic Carbons



Combustion of Alkanes

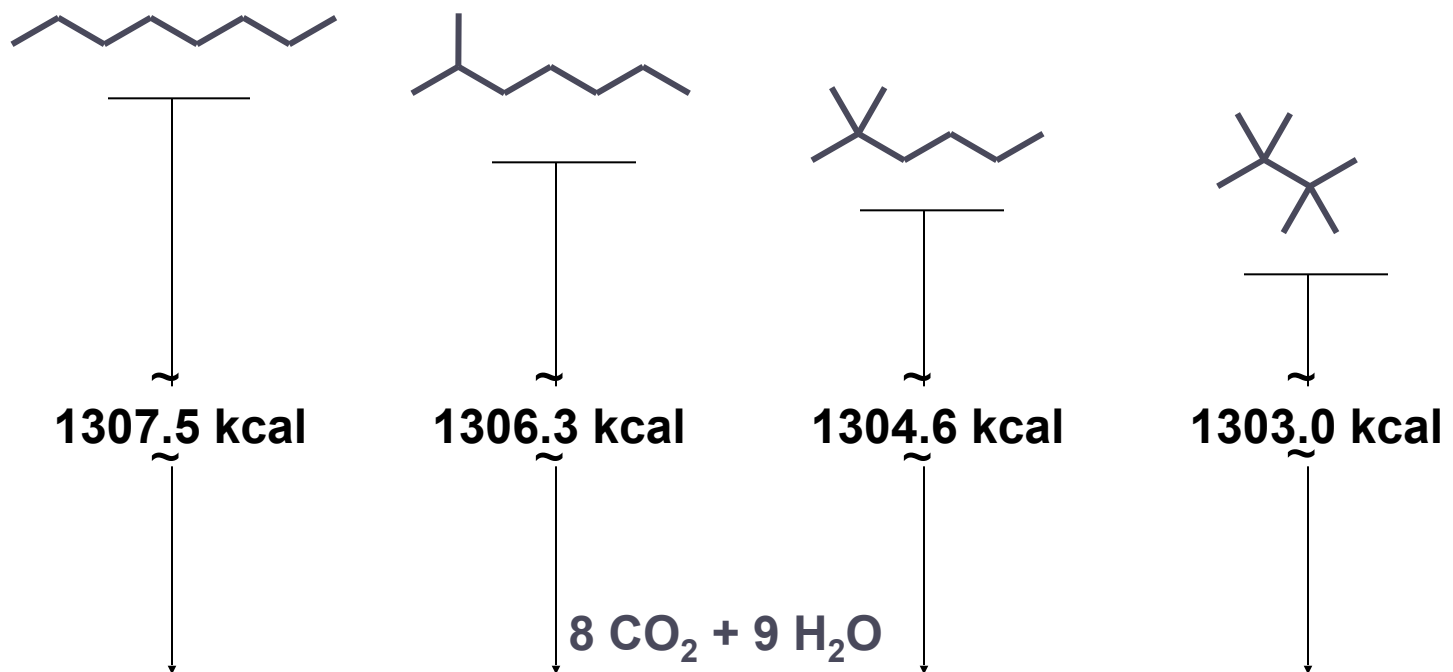
- ❑ Combustion is a redox reaction. C is oxidized and O is reduced.
- ❑ All hydrocarbons burn giving carbon dioxide, water and heat ($\Delta H < 0$).
- ❑ C-C e C-H bonds are converted into C-O and H-O bonds.



Every C atom is converted into CO_2

Stability of Isomers

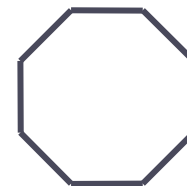
- Heats of combustion are used to compare the stability of isomers. E.g.: C_8H_{18}






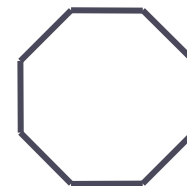


Branched isomers are more stable than linear ones.

Strain Energies of Cycloalkanes

- Heats of combustion are used to calculate strain energies of cycloalkanes.
- Heats of combustion increase with the number of C atoms.
- Cyclohexane is taken as reference (Strain = 0).



						
kJ/mol	2091	2724	3290	3910	4599	5264
Per CH ₂	697	681	658	653	657	658
Strain	132	112	25	0	28	40