3. Organic Compounds: Alkanes and Their Stereochemistry

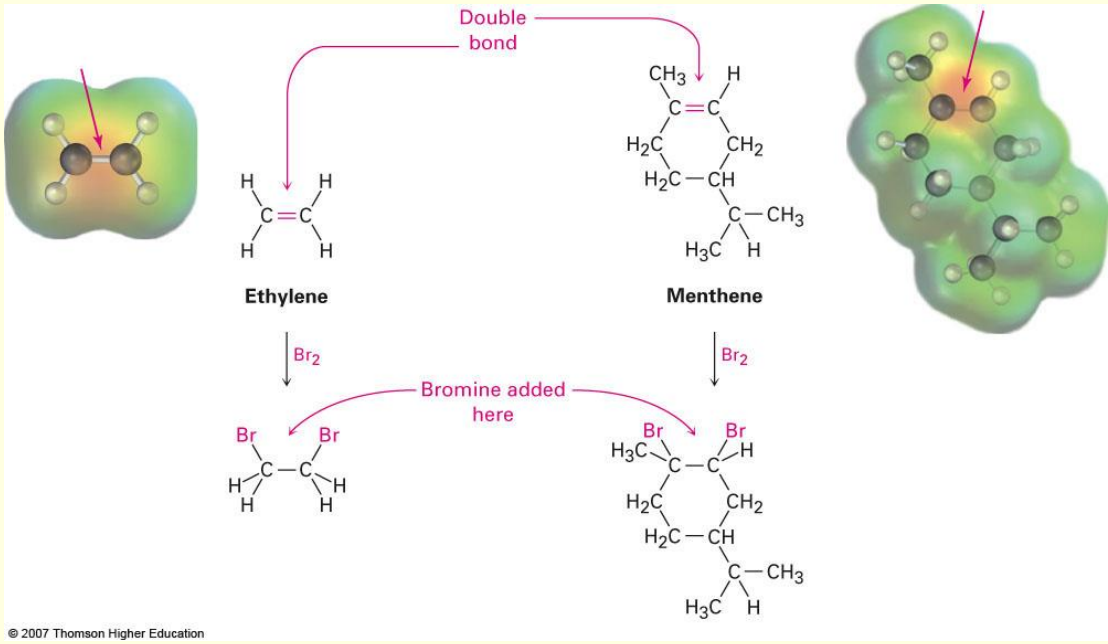
Based on McMurry's *Organic Chemistry*, 7th edition

Why this Chapter

- Alkanes are unreactive, but provide useful vehicle to introduce important ideas about organic compounds
- Alkanes will be used to discuss basic approaches to naming organic compounds
- We will take an initial look at 3-D aspects of molecules

3.1 Functional Groups

- **Functional group** - collection of atoms at a site that have a characteristic behavior in all molecules where it occurs

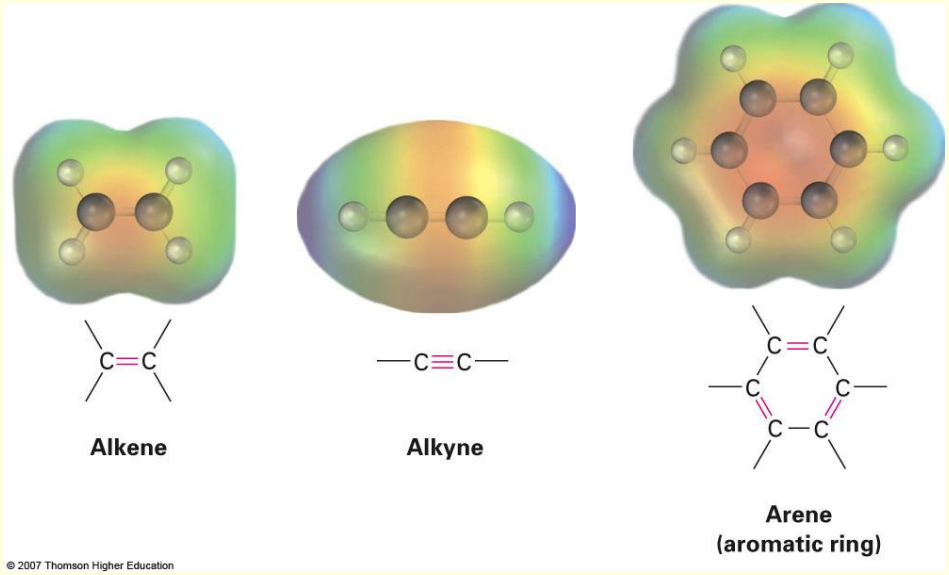


- The group reacts in a typical way, generally independent of the rest of the molecule

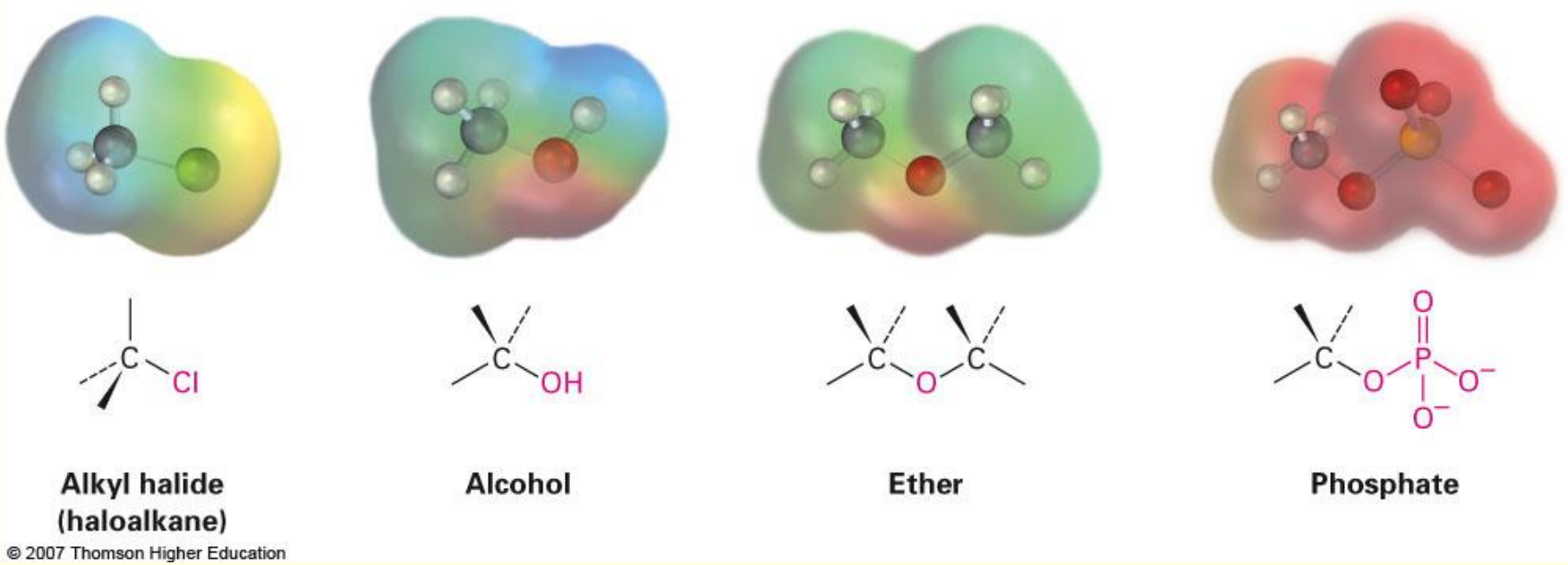
- For example, the double bonds in simple and complex alkenes react with bromine in the same way

Functional Groups with Multiple Carbon–Carbon Bonds

- *Alkenes* have a C-C double bond
- *Alkynes* have a C-C triple bond
- *Arenes* have special bonds that are represented as alternating single and double C-C bonds in a six-membered ring

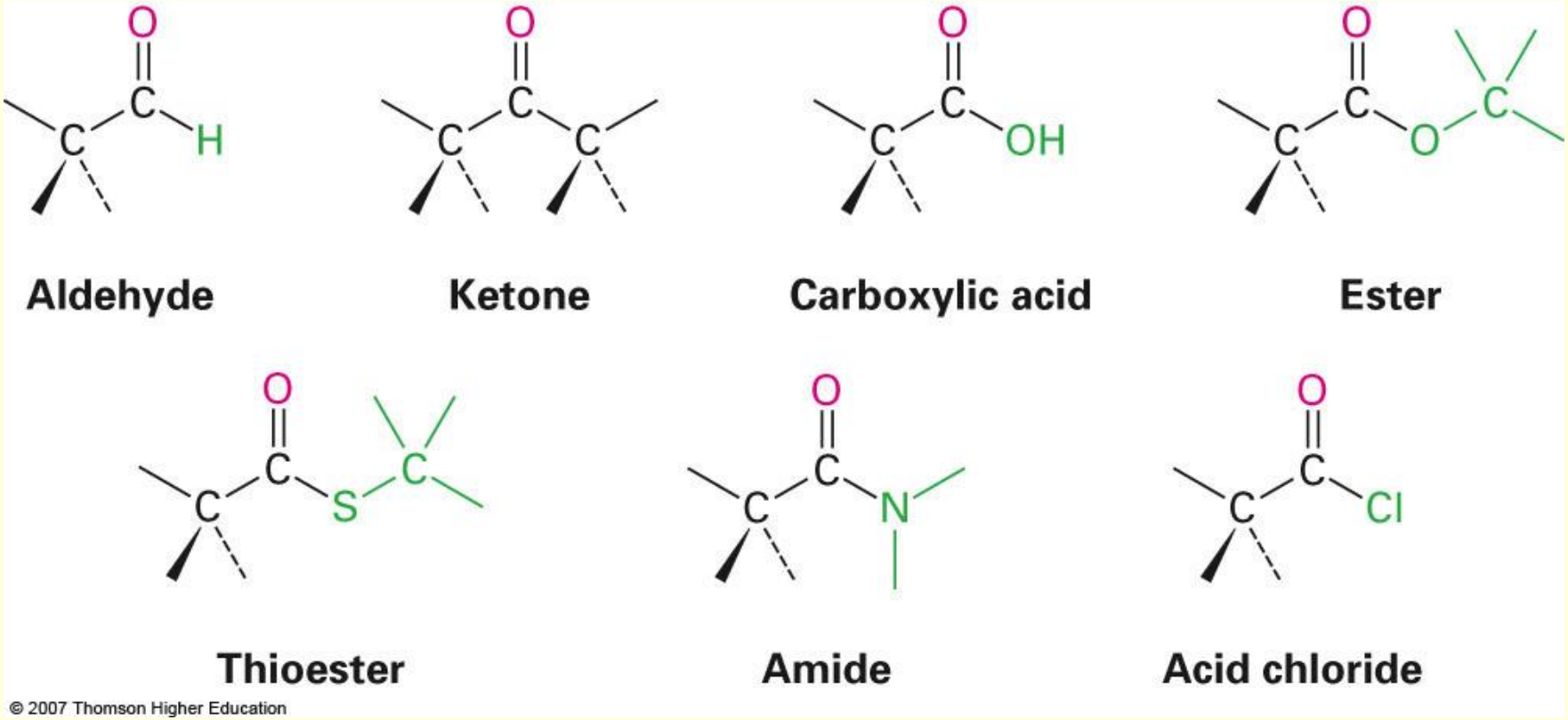


Functional Groups with Carbon Singly Bonded to an Electronegative Atom



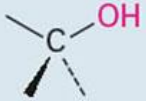
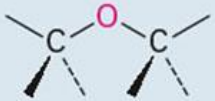
Alkyl halide (haloalkane) | **Alcohol** | **Ether** | **Phosphate**

Groups with a Carbon–Oxygen Double Bond (Carbonyl Groups)



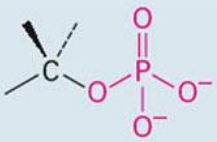
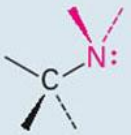
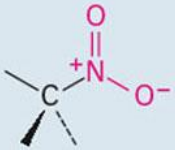
Survey of Functional Groups

Table 3.1 Structures of Some Common Functional Groups

Name	Structure*	Name ending	Example
Alkene (double bond)		*-ene*	$H_2C{=}CH_2$ Ethene
Alkyne (triple bond)		*-yne*	HC≡CH Ethyne
Arene (aromatic ring)		None	 Benzene
Halide	 (X = F, Cl, Br, I)	None	CH_3Cl Chloromethane
Alcohol		*-ol*	CH_3OH Methanol
Ether		*ether*	CH_3OCH_3 Dimethyl ether

Survey of Functional Groups

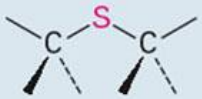
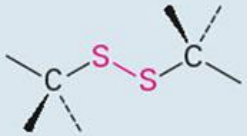
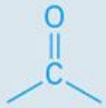
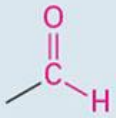
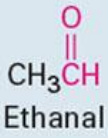
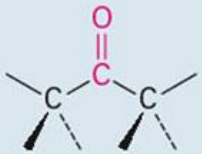
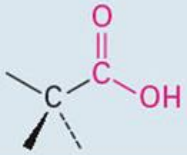
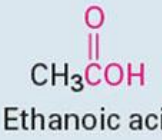
Table 3.1 Structures of Some Common Functional Groups *(continued)*

Name	Structure*	Name ending	Example
Monophosphate		*phosphate*	$CH_3OPO_3^{2-}$ Methyl phosphate
Amine		*-amine*	CH_3NH_2 Methylamine
Imine (Schiff base)		None	CH_3CCH_3 (=NH) Acetone imine
Nitrile	$-C\equiv N$	*-nitrile*	$CH_3C\equiv N$ Ethanenitrile
Nitro		None	CH_3NO_2 Nitromethane
Thiol		*-thiol*	CH_3SH Methanethiol

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

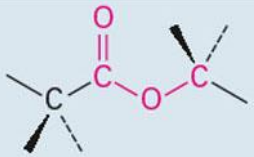
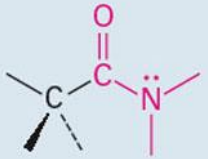
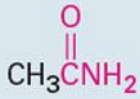
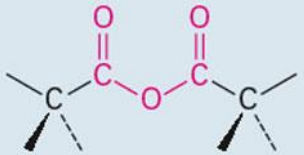
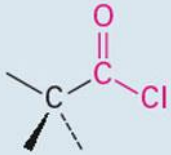
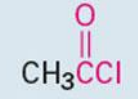
Survey of Functional Groups

Table 3.1 Structures of Some Common Functional Groups *(continued)*

Name	Structure*	Name ending	Example
Sulfide		*sulfide*	CH_3SCH_3 Dimethyl sulfide
Disulfide		*disulfide*	CH_3SSCH_3 Dimethyl disulfide
Carbonyl			
Aldehyde		*-al*	 Ethanal
Ketone		*-one*	 Propanone
Carboxylic acid		*-oic acid*	 Ethanoic acid

Survey of Functional Groups

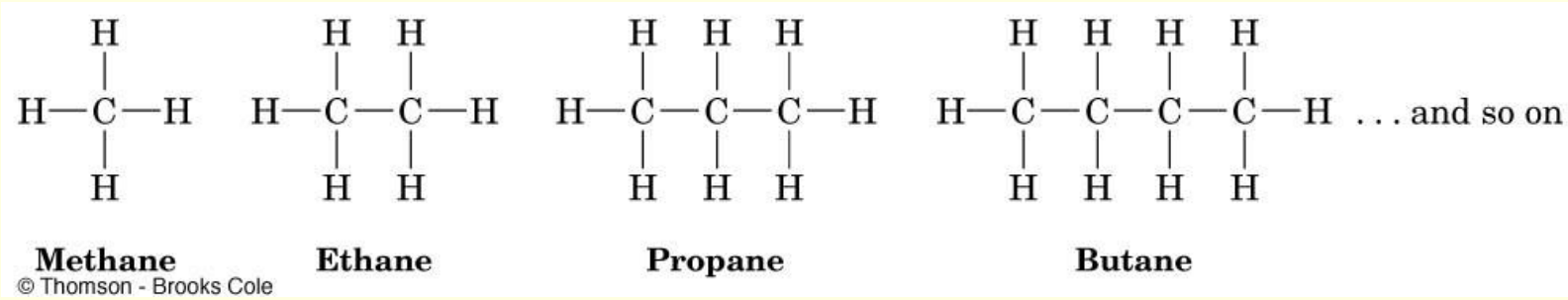
Table 3.1 Structures of Some Common Functional Groups

Name	Structure*	Name ending	Example
Ester		*-oate*	 Methyl ethanoate
Amide		*-amide*	 Ethanamide
Carboxylic acid anhydride		*-oic anhydride*	 Ethanoic anhydride
Carboxylic acid chloride		*-oyl chloride*	 Ethanoyl chloride

*The bonds whose connections aren't specified are assumed to be attached to carbon or hydrogen atoms in the rest of the molecule.

3.2 Alkanes and Alkane Isomers

- Alkanes: Compounds with C-C single bonds and C-H bonds only (no functional groups)
- Connecting carbons can lead to large or small molecules
- The formula for an alkane with no rings in it must be C_nH_{2n+2} where the number of C's is n
- Alkanes are **saturated** with hydrogen (no more can be added
- They are also called **aliphatic compounds**



Alkane Isomers

- CH_4 = methane, C_2H_6 = ethane, C_3H_8= propane
- The molecular formula of an alkane with more than three carbons can give more than one structure
  - C_4 (butane) = butane and isobutane
  - C_5 (pentane) = pentane, 2-methylbutane, and 2,2-dimethylpropane
- Alkanes with C's connected to no more than 2 other C's are **straight-chain** or **normal alkanes**
- Alkanes with one or more C's connected to 3 or 4 C's are **branched-chain alkanes**

Constitutional Isomers

- Isomers that differ in how their atoms are arranged in chains are called **constitutional isomers**
- Compounds other than alkanes can be **constitutional isomers** of one another
- They must have the same molecular formula to be isomers

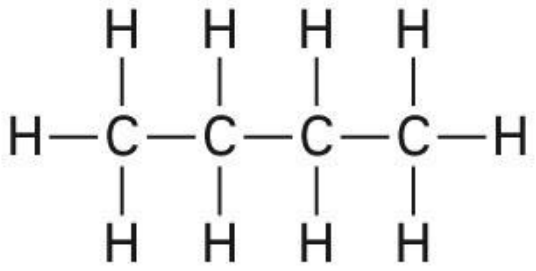
Table 3.2 Number of Alkane Isomers

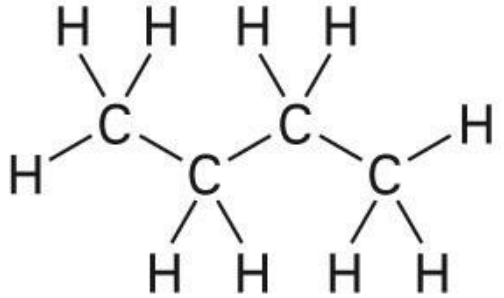
Formula	Number of isomers
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	4,347
$C_{20}H_{42}$	366,319
$C_{30}H_{62}$	4,111,846,763

Different carbon skeletons C_4H_{10}	$CH_3CH(CH_3)CH_3$	and	$CH_3CH_2CH_2CH_3$
	2-Methylpropane (isobutane)		**Butane**
Different functional groups C_2H_6O	CH_3CH_2OH	and	CH_3OCH_3
	Ethanol		**Dimethyl ether**
Different position of functional groups C_3H_9N	$CH_3CH(NH_2)CH_3$	and	$CH_3CH_2CH_2NH_2$
	Isopropylamine		**Propylamine**

Condensed Structures of Alkanes

- We can represent an alkane in a brief form or in many types of extended form
- A condensed structure does not show bonds but lists atoms, such as
  - $CH_3CH_2CH_2CH_3$ (butane)
  - $CH_3(CH_2)_2CH_3$ (butane)





$CH_3—CH_2—CH_2—CH_3$ $CH_3CH_2CH_2CH_3$ $CH_3(CH_2)_2CH_3$

Table 3.3 Names of Straight-Chain Alkanes

Number of carbons (n)	Name	Formula (C_nH_{2n+2})
1	Methane	CH_4
2	Ethane	C_2H_6
3	Propane	C_3H_8
4	Butane	C_4H_{10}
5	Pentane	C_5H_{12}
6	Hexane	C_6H_{14}
7	Heptane	C_7H_{16}
8	Octane	C_8H_{18}
9	Nonane	C_9H_{20}
10	Decane	$C_{10}H_{22}$
11	Undecane	$C_{11}H_{24}$
12	Dodecane	$C_{12}H_{26}$
13	Tridecane	$C_{13}H_{28}$
20	Icosane	$C_{20}H_{42}$
30	Triacontane	$C_{30}H_{62}$

3.3 Alkyl Groups

- **Alkyl group** – remove one H from an alkane (a part of a structure)
- General abbreviation “R” (for Radical, an incomplete species or the “rest” of the molecule)
- Name: replace -*ane* ending of alkane with -*yl* ending
  - CH_3 is “methyl” (from methane)
  - CH_2CH_3 is “ethyl” from ethane

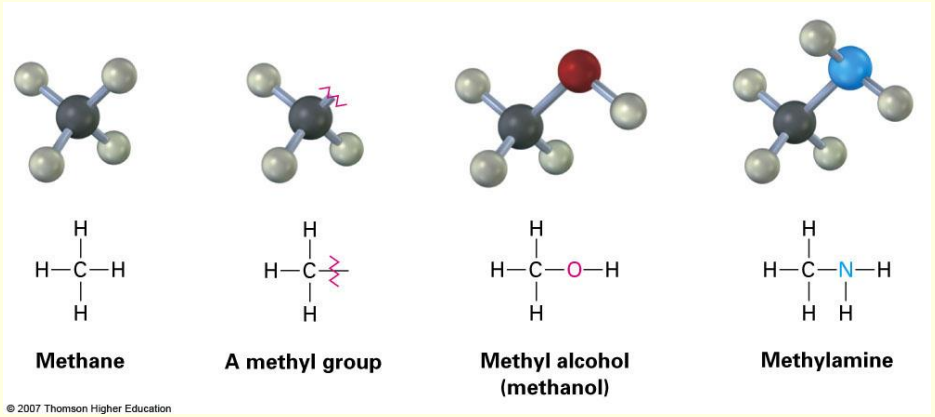
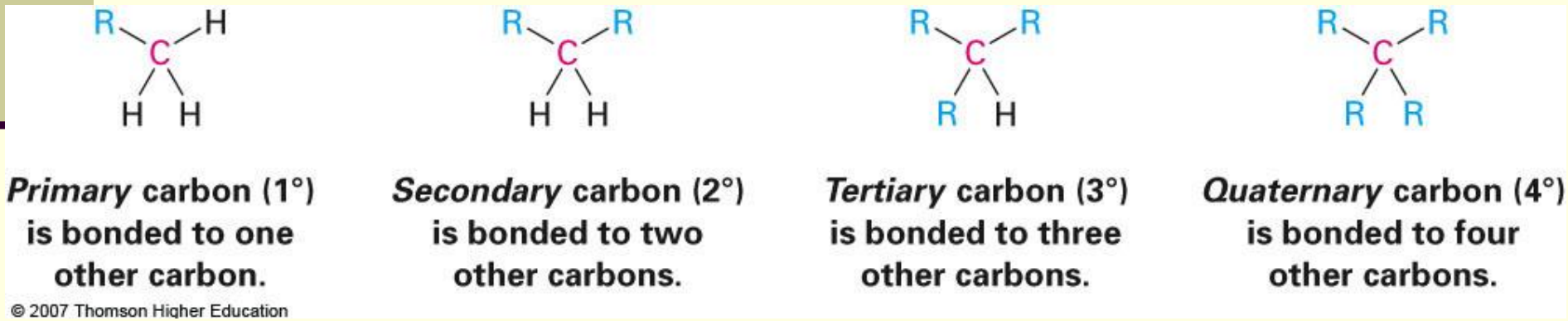


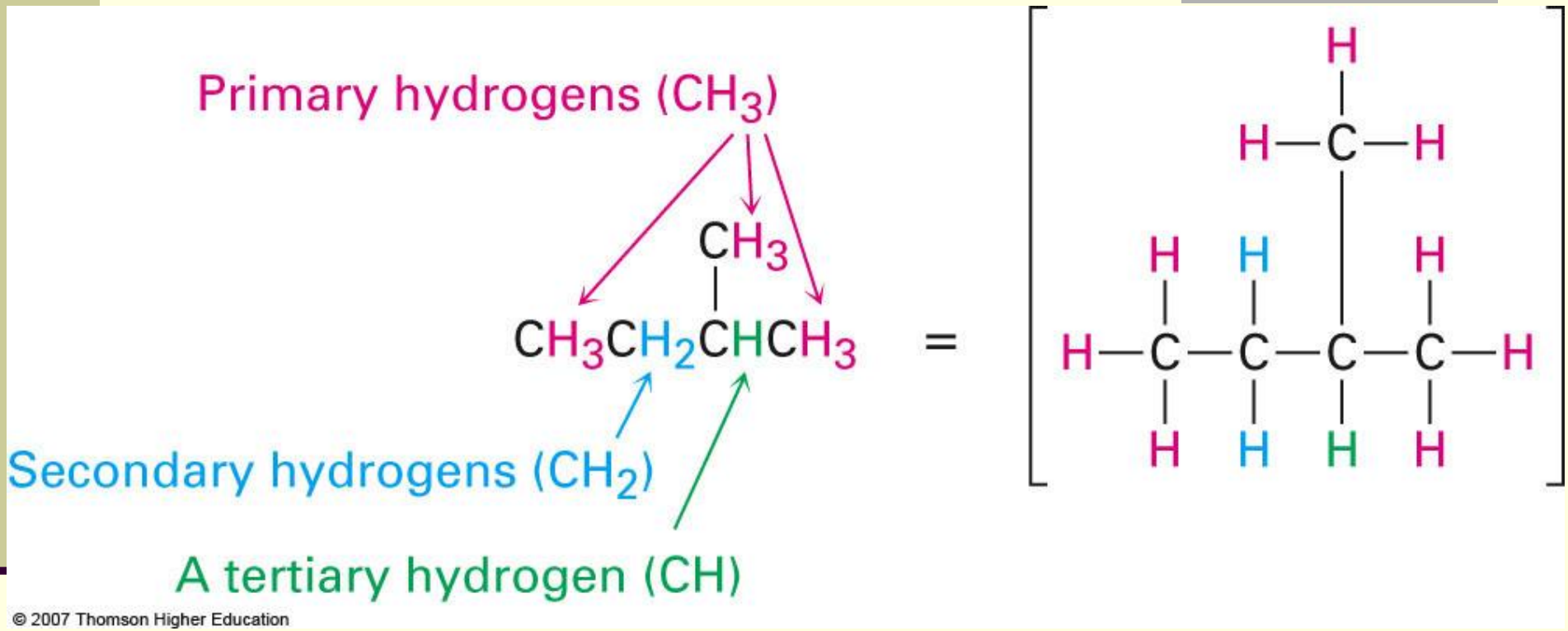
Table 3.4 Some Straight-Chain Alkyl Groups

Alkane	Name	Alkyl group	Name (abbreviation)
CH_4	Methane	$-CH_3$	Methyl (Me)
CH_3CH_3	Ethane	$-CH_2CH_3$	Ethyl (Et)
$CH_3CH_2CH_3$	Propane	$-CH_2CH_2CH_3$	Propyl (Pr)
$CH_3CH_2CH_2CH_3$	Butane	$-CH_2CH_2CH_2CH_3$	Butyl (Bu)
$CH_3CH_2CH_2CH_2CH_3$	Pentane	$-CH_2CH_2CH_2CH_2CH_3$	Pentyl, or amyl

Types of Alkyl groups

- Classified by the connection site (See Figure 3.3)
  - a carbon at the end of a chain (primary alkyl group)
  - a carbon in the middle of a chain (secondary alkyl group)
  - a carbon with three carbons attached to it (tertiary alkyl group)





3.4 Naming Alkanes

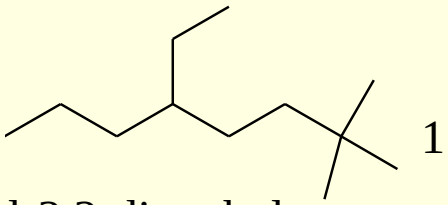
- Compounds are given systematic names by a process that uses

- Follows specific rules
  - Find parent hydrocarbon chain
  - Carbons in that main chain are numbered in sequence
  - Substituents are identified numbered
  - Write compound name is single word
  - Name a complex substituents as though it were a compound itself
- See specific examples in text
- Try ThomsonNow Organic Interactive from p. 90 of your text

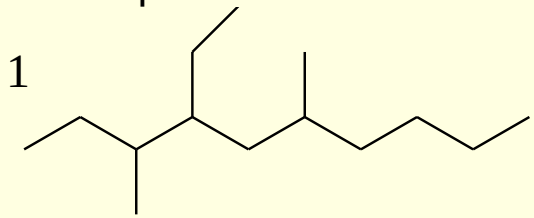
Rules for naming Branched Alkanes (or drawing structure from name)

- Find the longest chain and name it as a straight chain alkane
- Name substituents as alkyl groups

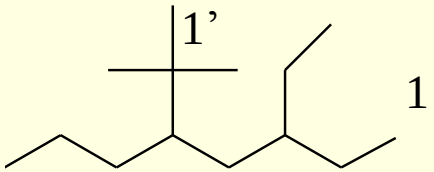
- Number the main chain starting from the end closest to a substituent
- Write the name
  - Alphabetize by sub. (di-, tri-count only if part of sub. name)
  - Order #'s from low to high; use smallest possible numbers
  - Capitalize the first letter only
  - Write as one word with commas and hyphens as needed
  - Complex substituents in parentheses



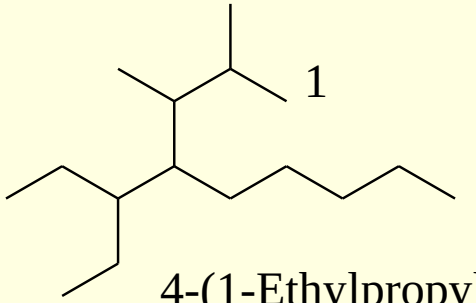
5-Ethyl-2,2-dimethyloctane



4-ethyl-3,6-dimethyldecane



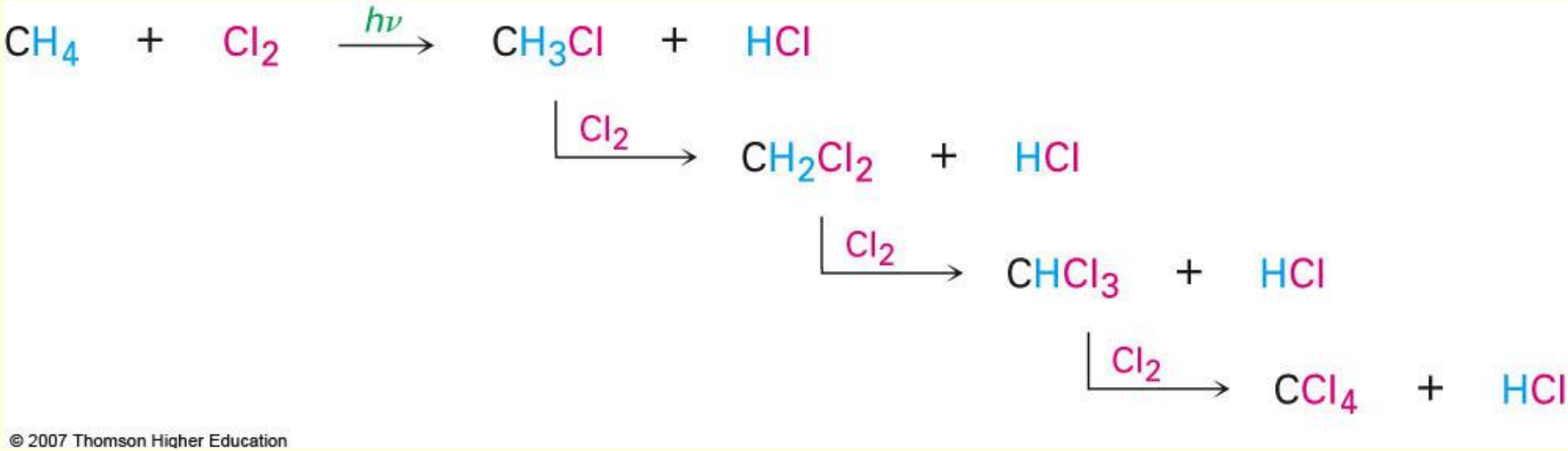
5-(1,1-Dimethylethyl)-3-ethyloctane



4-(1-Ethylpropyl)-2,3-dimethylnonane

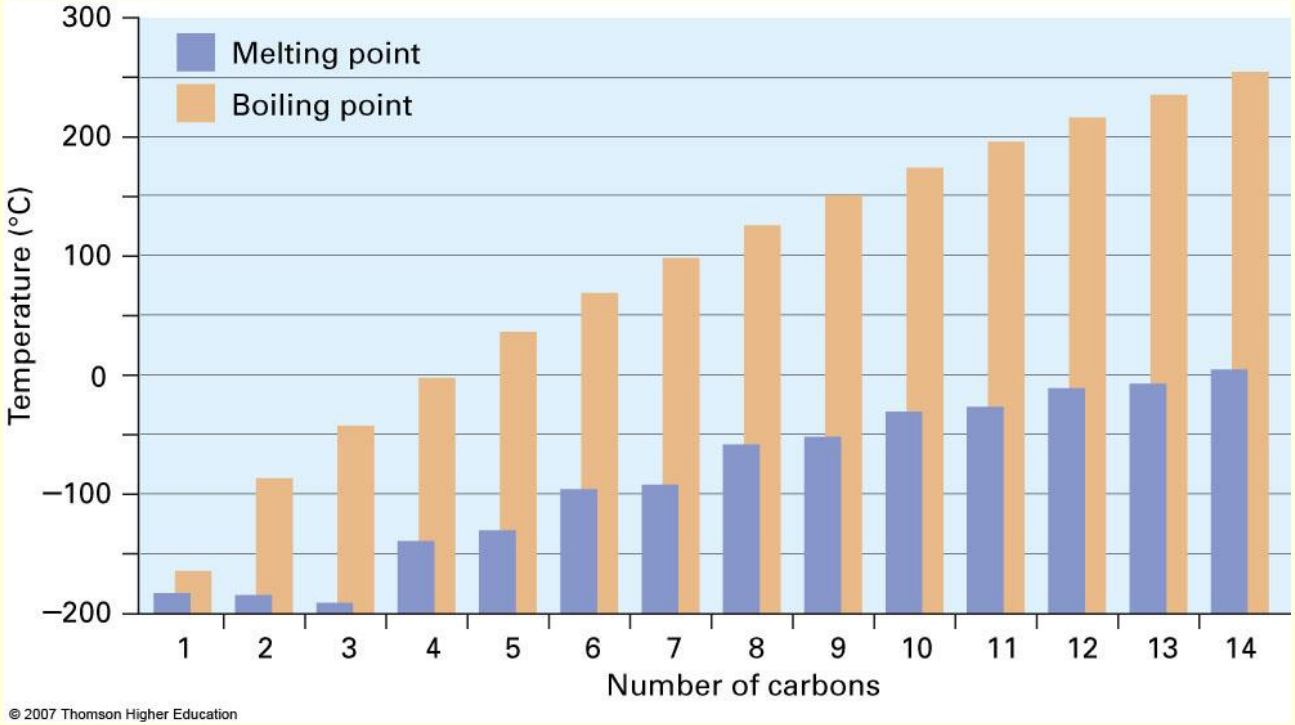
3.5 Properties of Alkanes

- Called **paraffins** (low affinity compounds) because they do not react as most chemicals
- They will burn in a flame, producing carbon dioxide, water, and heat
- They react with Cl_2 in the presence of light to replace H's with Cl's (not controlled)



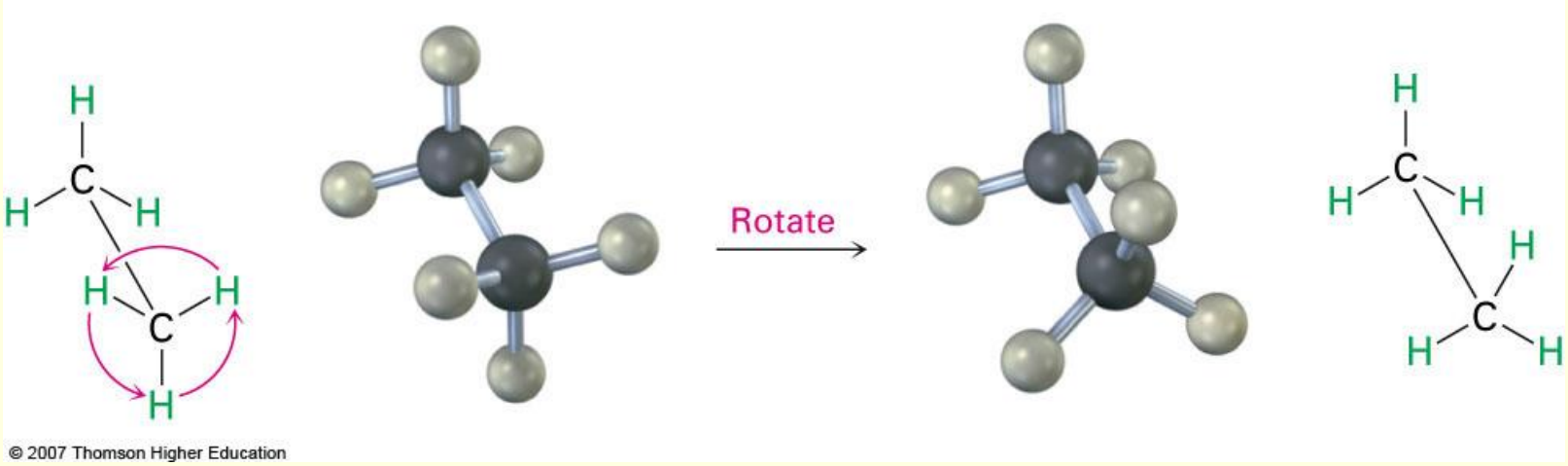
Physical Properties

- Boiling points and melting points increase as size of alkane increases
- Dispersion forces increase as molecule size increases, resulting in higher melting and boiling points



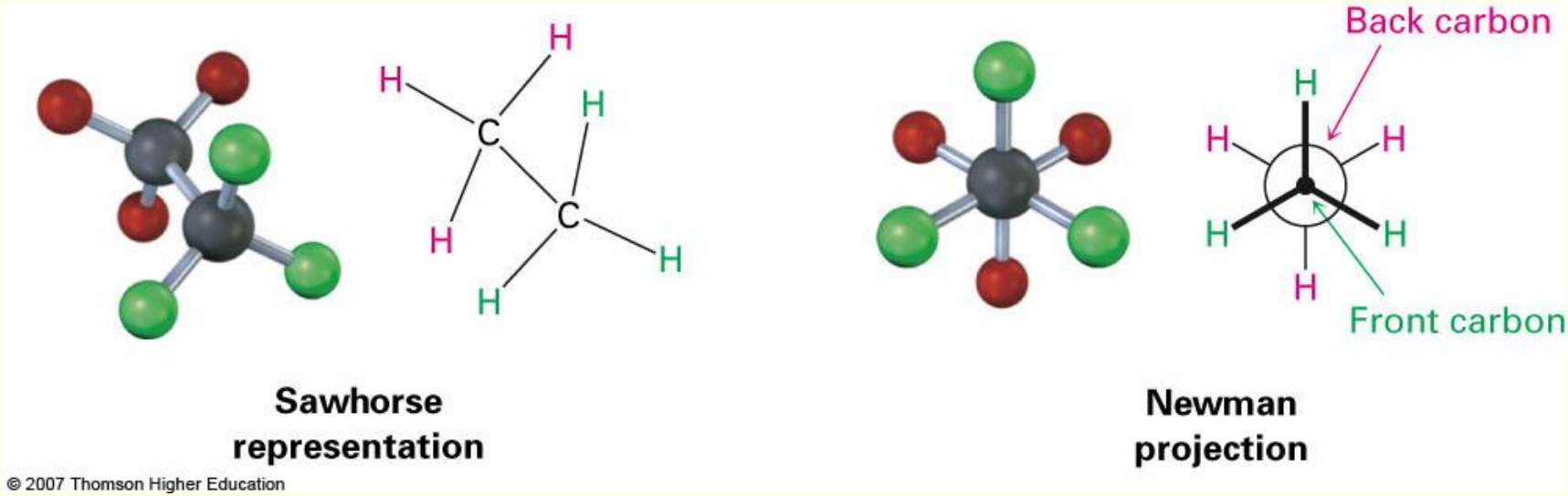
3.6 Conformations of Ethane

- Stereochemistry concerned with the 3-D aspects of molecules
- σ bonds are cylindrically symmetrical
- Rotation is possible around C-C bonds in open-chain molecules



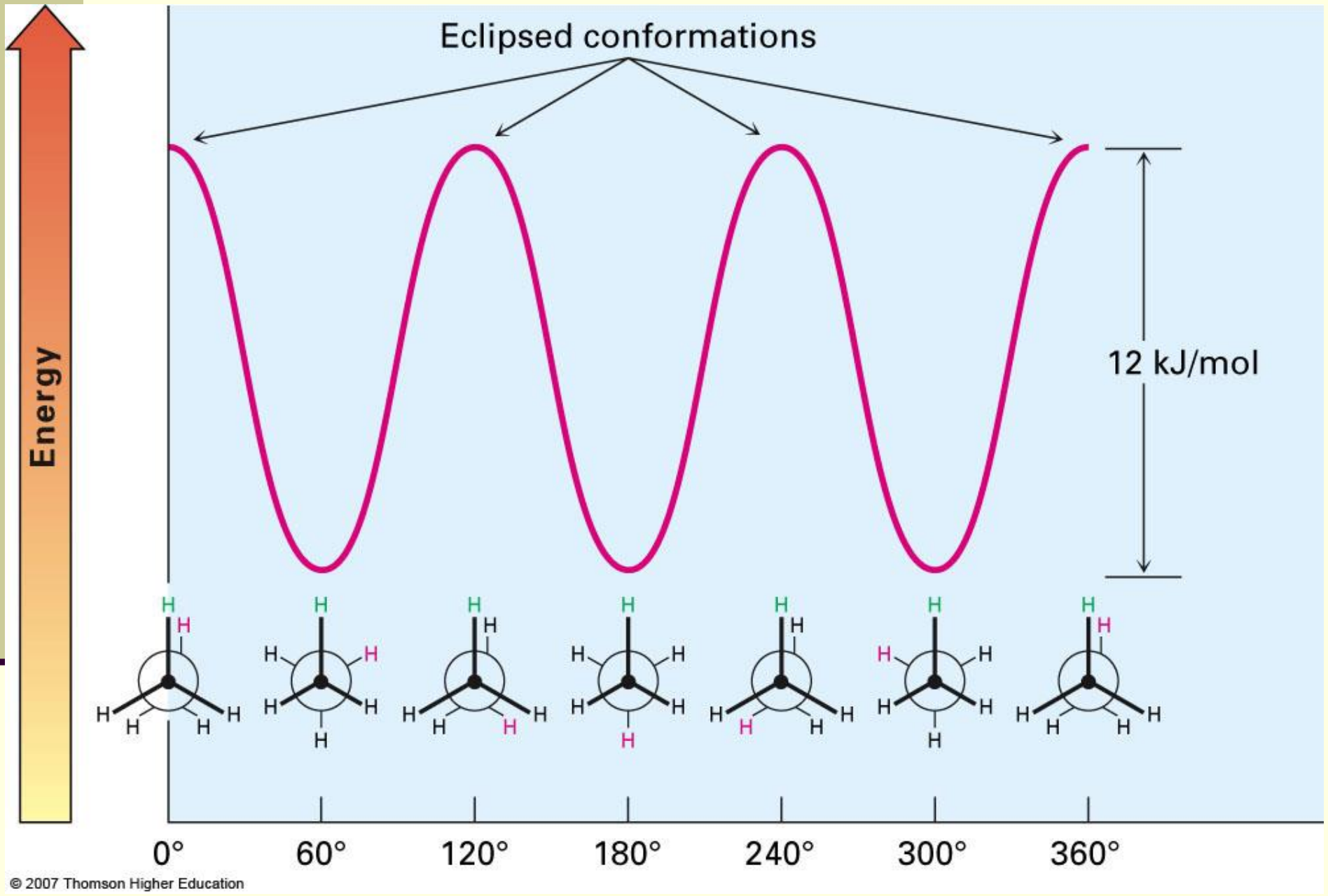
Conformers

- **Conformation**- Different arrangement of atoms resulting from bond rotation
- Conformations can be represented in 2 ways:



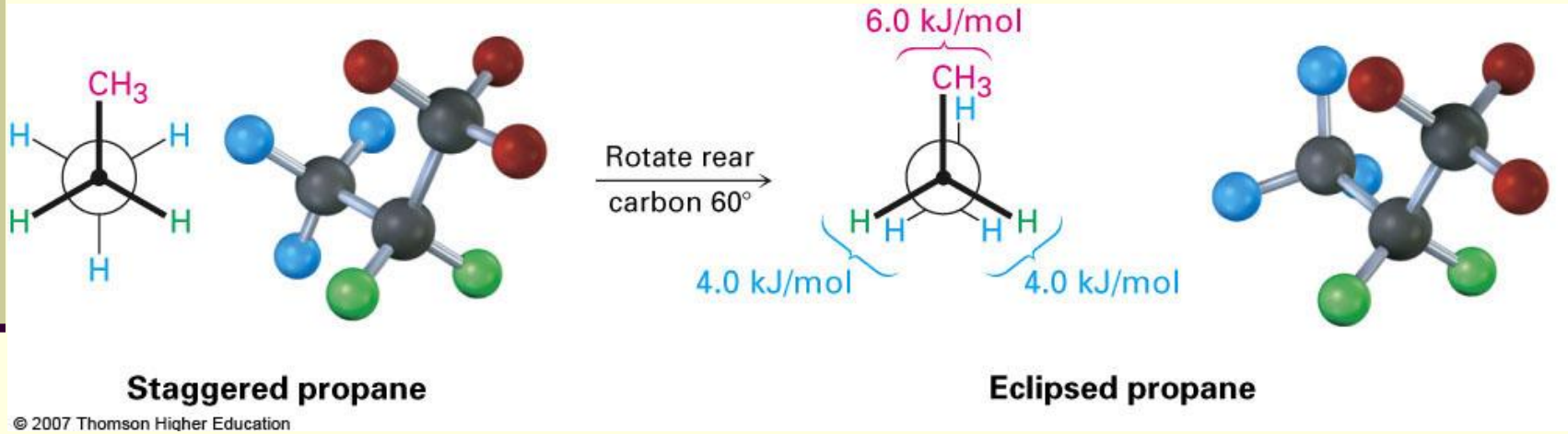
Torsional Strain

- We do not observe perfectly free rotation
- There is a barrier to rotation, and some conformers are more stable than others
- **Staggered**- most stable: all 6 C-H bonds are as far away as possible
- **Eclipsed**- least stable: all 6 C-H bonds are as close as possible to each other


Eclipsed conformations
Energy
12 kJ/mol
0°
60°
120°
180°
240°
300°
360°
© 2007 Thomson Higher Education

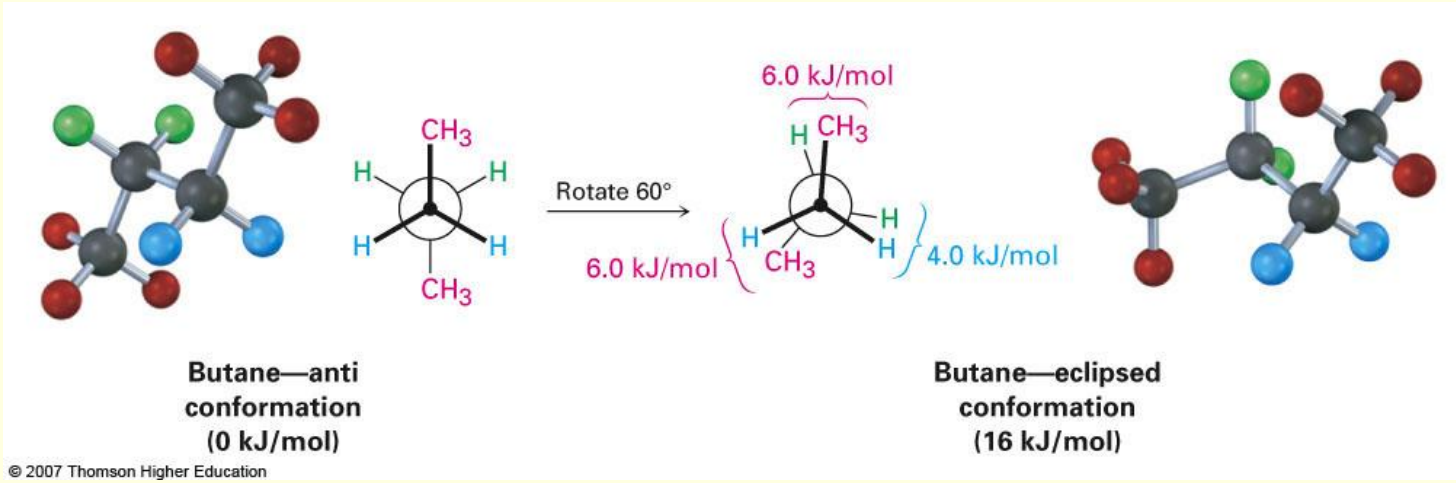
3.7 Conformations of Other Alkanes

- The eclipsed conformer of propane has 3 interactions: two ethane-type H-H interactions, and one H-CH_3 interaction



Conformations of Other Alkanes

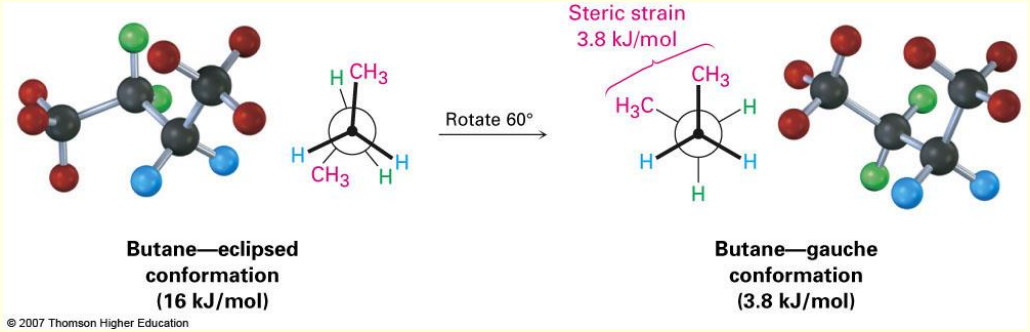
- Conformational situation is more complex for larger alkanes
- Not all staggered conformations has same energy, and not all eclipsed conformations have same energy

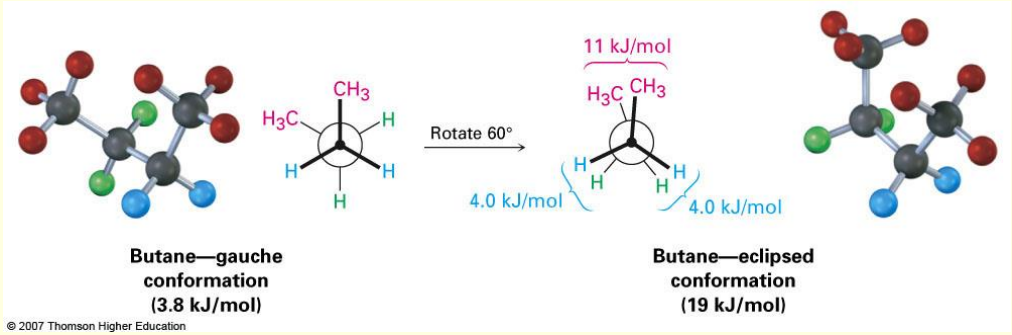


Conformations of Butane

- **Anti** conformation- methyl groups are 180˚ apart
- **Gauche** conformation- methyl groups are 60˚ apart

Which is the most energetically stable?





Steric Strain

- **Steric strain-** repulsive interaction occurring between atoms that are forced closer together than their atomic radii allow

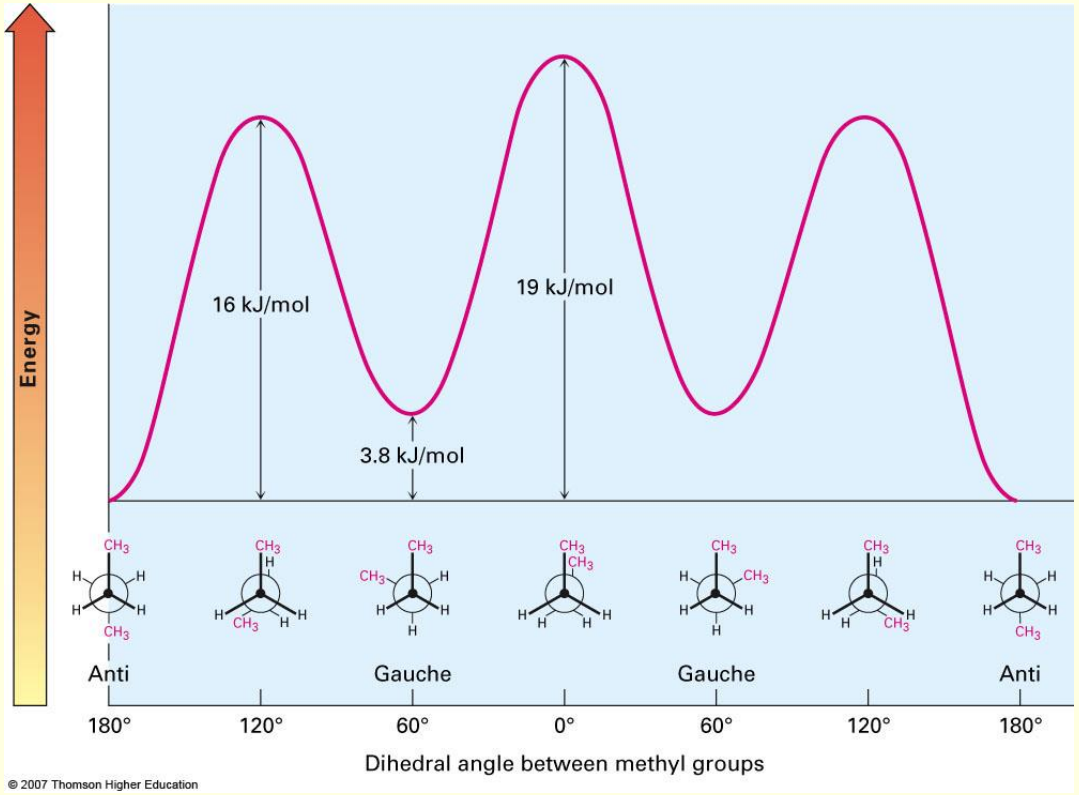


Table 3.5 Energy Costs for Interactions in Alkane Conformers

Interaction	Cause	Energy cost (kJ/mol)	Energy cost (kcal/mol)
H⟷H eclipsed	Torsional strain	4.0	1.0
H⟷CH_3 eclipsed	Mostly torsional strain	6.0	1.4
CH_3⟷CH_3 eclipsed	Torsional and steric strain	11	2.6
CH_3⟷CH_3 gauche	Steric strain	3.8	0.9