Last-chapter Review

❖ Lewis structures

➢ A structural formula that shows all valence electrons, with the bonds symbolized by dashes or by pairs of dots, and nonbonding electrons symbolized by dots.

❖ Resonance forms (and tautomerism)

➢ The different Lewis structures that are different only in the placement of electrons are called **resonance structures** or **resonance forms**. They are not different compounds, just different ways of drawing the same compound. The actual molecule is said to be a **resonance hybrid** of its resonance forms.

Last-chapter Review

❖ Hybridization: sp, sp^2, sp^3

➢ To explain the shapes of common organic molecules, we assume that the *s* and *p* orbitals combine to form hybrid atomic orbitals that separate the electron pairs more widely in space and place more electron density in the bonding region between the nuclei.

Last-chapter Review

❖ Electronic effect

- **Inductive effect** (+I, -I): A donation (or withdrawal) of electron density through sigma bonds caused by difference in electronegativity.
- **Conjugation effect** (+C, -C): Delocalization of electron density in a **conjugated system** – or a conjugated double bonds (Double bonds that alternate with single bonds, with interaction by overlap of the *p* orbitals in the pi bonds).
- **Hyperconjugation** (+H, -H): overlap between a *p* orbital and a sigma bond.

Last-chapter Review

❖ Reactive intermediates

- **Reactive intermediates** are short-lived species that is never present in high concentration because it reacts as quickly as it is formed. They are generally unstable.
- **Carbocation:** **(carbonium ion, carbenium ion)** A strongly electrophilic species with a positively charged carbon atom having only three bonds.
- **Carbanion:** A strongly nucleophilic species with a negatively charged carbon atom having only three bonds. The carbon atom has a nonbonding pair of electrons.
- **Free radical** possesses a single unshared electron.

Last-chapter Review

❖ Weak intermolecular interaction

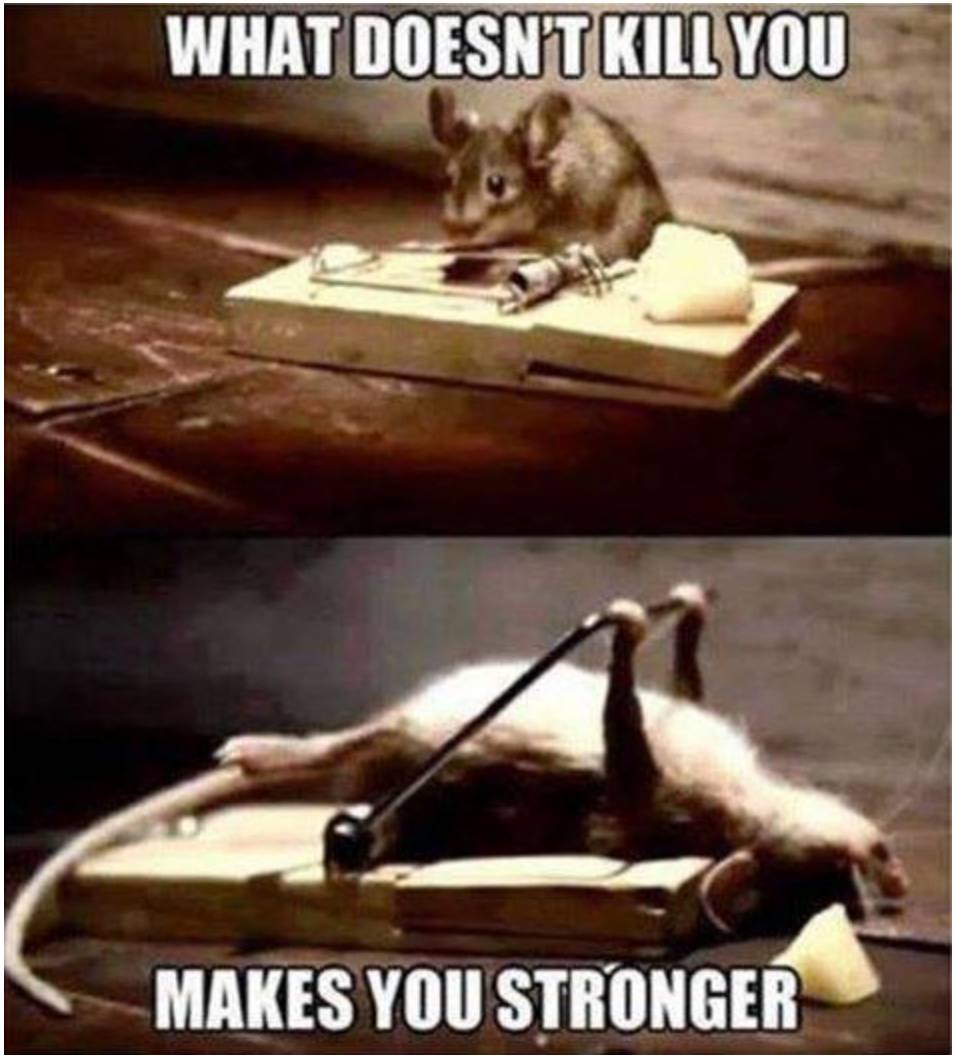
- **Van der Waals attraction** include:

+ The dipole-dipole forces of polar molecules (having permanent dipole moments); and

+ The dispersion (London) forces that affect all molecules. This arises from temporary dipole moments. These temporary dipoles last only a fraction of a second, and they constantly change; yet they are correlated so their net force is attractive. This attractive force depends on close surface contact of two molecules, so it is roughly proportional to the molecular surface area.

- **Hydrogen bonds** link molecules having –OH or –NH groups.

- Attractions between molecules strongly affect the melting points, boiling points, and solubilities of organic compounds.



Kelly Clarkson

Never give up!

Chapter 3

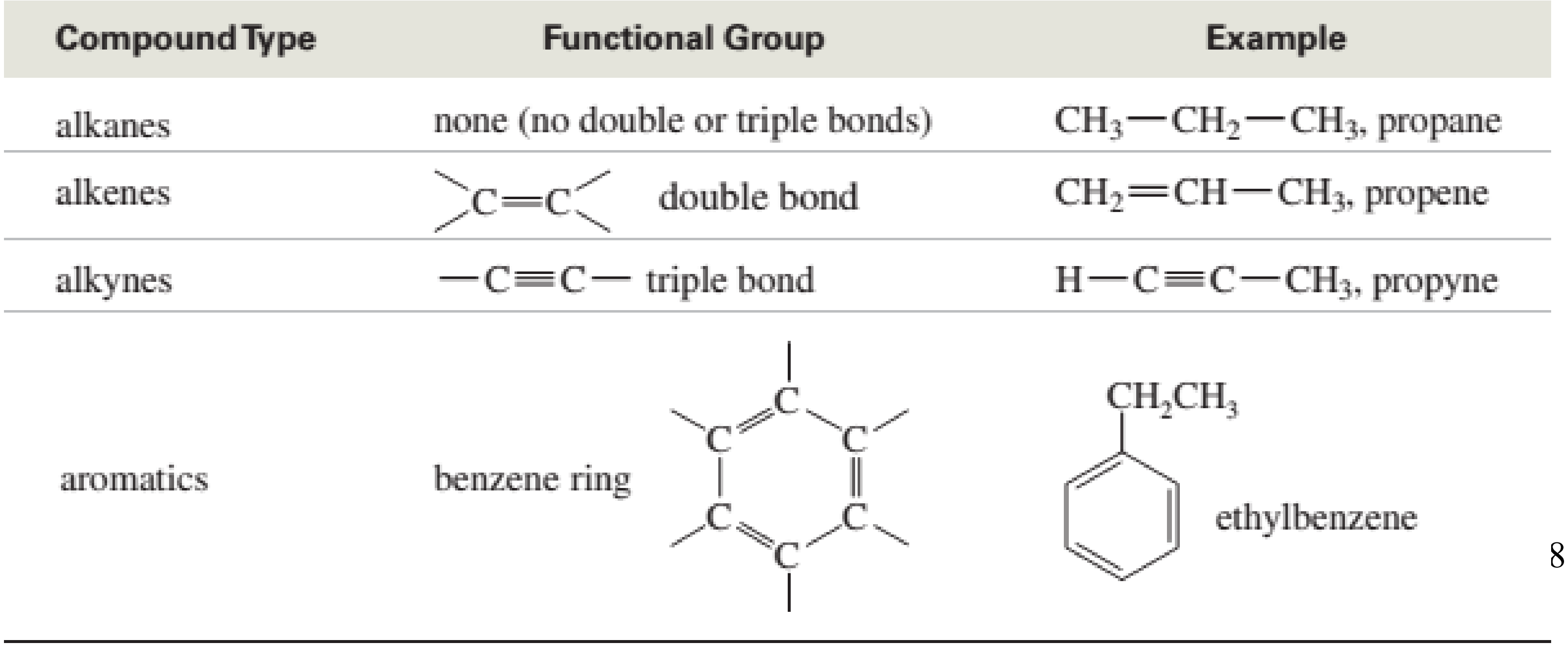
Part I

Alkanes

Nomenclature, properties, and an introduction to synthesis

Classification of hydrocarbons

- **Hydrocarbons** are organic compounds that contains only **carbon** and **hydrogen**.
  - We classify hydrocarbons according to their bonding, as shown in the Table below.
  + **Alkanes** have only **single** bonds.
  + A hydrocarbon with a carbon–carbon **double** bond (such as ethylene) is an ***alkene***.
  + If a hydrocarbon has a carbon–carbon **triple** bond (like acetylene), it is an ***alkyne***.
  + Hydrocarbons with aromatic rings (resembling benzene) are called ***aromatic hydrocarbons***.



Compound Type	Functional Group	Example
alkanes	none (no double or triple bonds)	$CH_3-CH_2-CH_3$, propane
alkenes	$>C=C<$ double bond	$CH_2=CH-CH_3$, propene
alkynes	$-C\equiv C-$ triple bond	$H-C\equiv C-CH_3$, propyne
aromatics	benzene ring	CH_2CH_3 ethylbenzene

Molecular formulas of alkanes

- If the molecule contains *n* carbon atoms, it must contain (2n+2) hydrogen atoms: C_nH_{2n+2}, with n= 1, 2, 3, …

➢ A series of compounds, like the unbranched alkanes, that differ only by the number of groups, is called a -CH_2- ***homologous*** *series*, and the individual members of the series are called **homologs**.

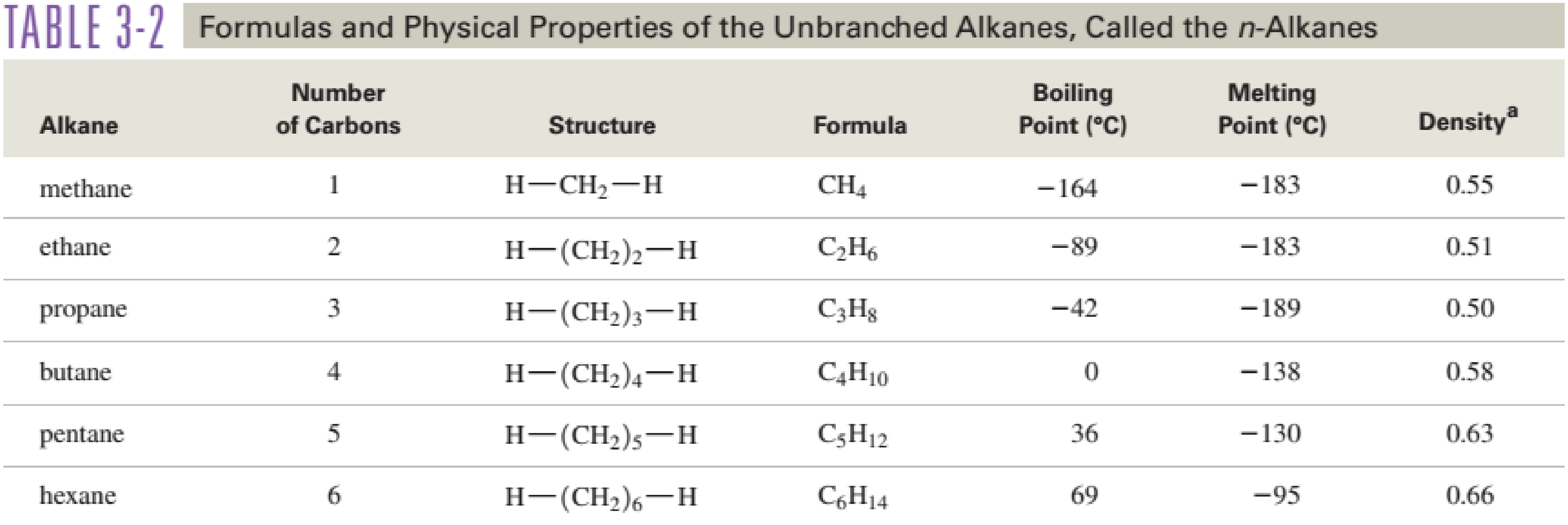
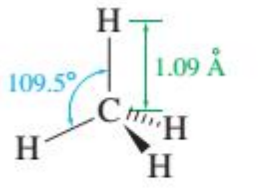


TABLE 3-2 Formulas and Physical Properties of the Unbranched Alkanes, Called the *n*-Alkanes

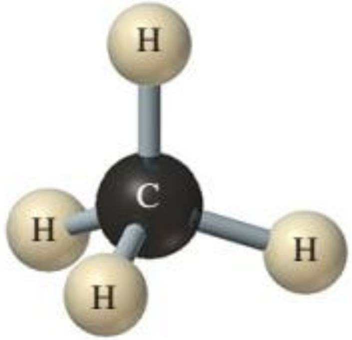
Alkane	Number of Carbons	Structure	Formula	Boiling Point (°C)	Melting Point (°C)	Density[a]
methane	1	$H{-}CH_2{-}H$	CH_4	−164	−183	0.55
ethane	2	$H{-}(CH_2)_2{-}H$	C_2H_6	−89	−183	0.51
propane	3	$H{-}(CH_2)_3{-}H$	C_3H_8	−42	−189	0.50
butane	4	$H{-}(CH_2)_4{-}H$	C_4H_{10}	0	−138	0.58
pentane	5	$H{-}(CH_2)_5{-}H$	C_5H_{12}	36	−130	0.63
hexane	6	$H{-}(CH_2)_6{-}H$	C_6H_{14}	69	−95	0.66

➢ Although we have derived the formula using the unbranched *n*-alkanes, it applies to branched alkanes as well.

Structures and conformation of alkanes

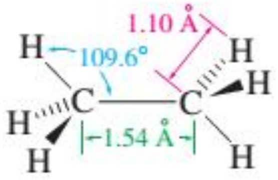


methane

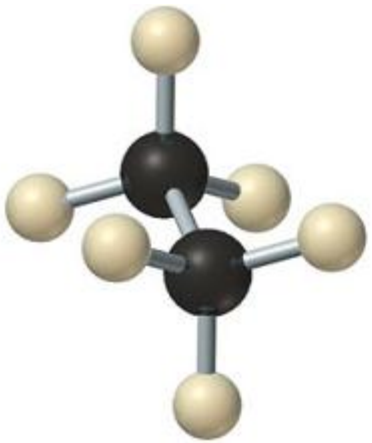


methane

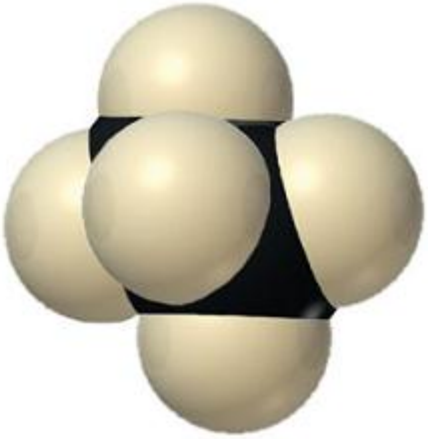
methane



ethane



ethane



ethane

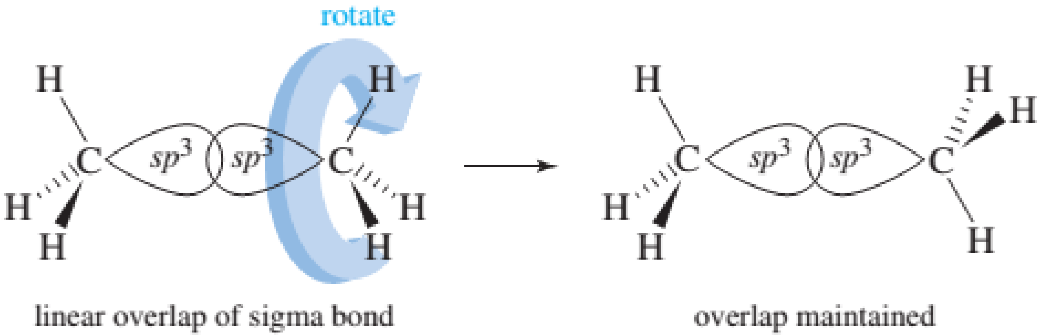
“Conformational isomer” - Conformers

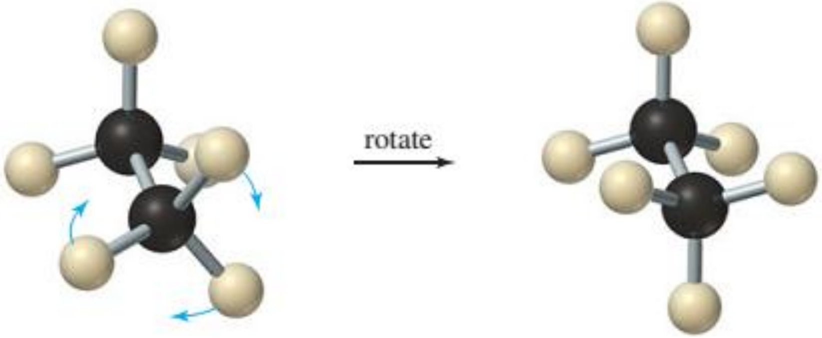
- The two methyl groups are not fixed in a single position but are relatively free to rotate about the sigma bond connecting the two carbon atoms.

➢ The bond maintains its linear bonding overlap as the carbon atoms turn.

- The different arrangements formed by rotations about a single bond are called **conformations,** and a specific conformation is called a **conformer** (“**confor**mational iso**mer**”).

➢ Pure conformers cannot be isolated in most cases, because the molecules are constantly rotating through all thepossible conformations.





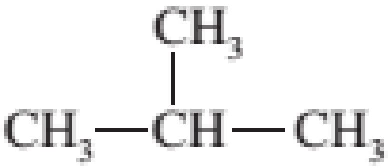
Constitutional isomerism

- **Constitutional isomers** (or **structural isomers**) are isomers that differ in their bonding sequence; that is, their atoms are connected differently.

- Either of the following structural formula would be correct for the molecular formula C_4H_{10}.

$CH_3—CH_2—CH_2—CH_3$

n-butane



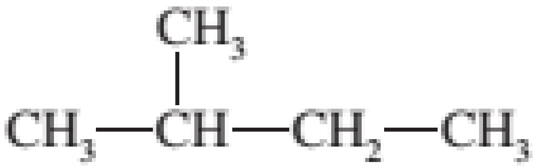
$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_3$$

isobutane

- There are three constitutional isomers of pentane.

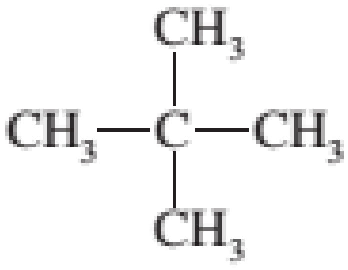
$CH_3—CH_2—CH_2—CH_2—CH_3$

n-pentane



$$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{CH}—CH_2—CH_3$$

isopentane

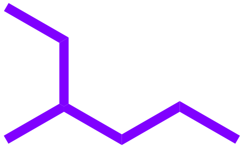


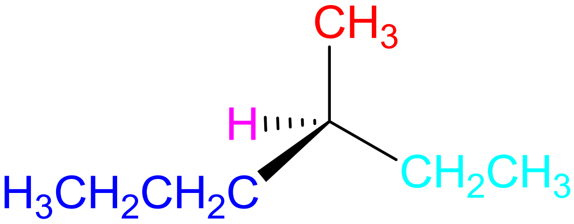
$$CH_3—\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}—CH_3$$

neopentane

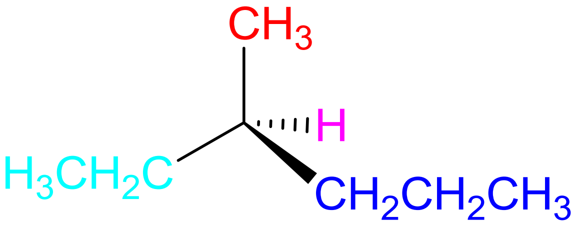
The number of isomers increases rapidly as the number of carbon atoms increases.

Stereoisomerism

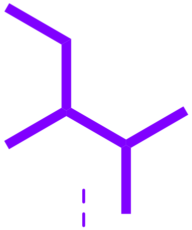


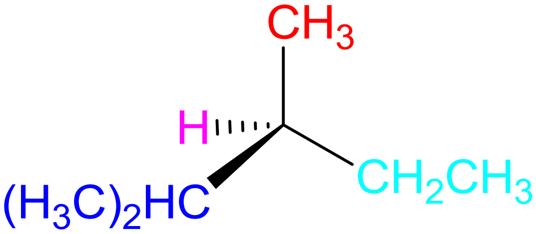


(*S*)-3-Methylhexane

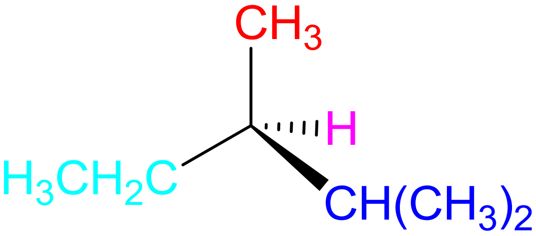


(*R*)-3-Methylhexane





(*S*)-2,3-Dimethylpentane



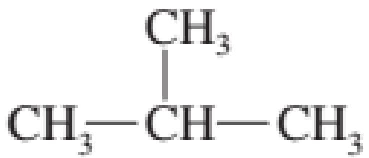
(*R*)-2,3-Dimethylpentane

Nomenclature of unbranched alkyl groups: Common names

- The names *methane*, *ethane*, *propane*, and *butane* have historical roots.
- From pentane on, alkanes are named using the Greek word for the number of carbon atoms (word root), plus the suffix -*ane* to identify the molecule as an alkane.

$CH_3-CH_2-CH_2-CH_3$

butane (*n*-butane)



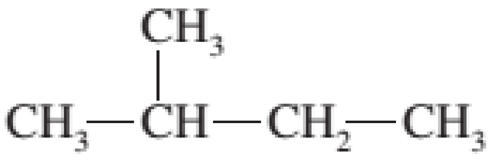
$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_3$

isobutane

- The three isomers of are called C_5H_{12} *pentane* (or *n-pentane*), *isopentane*, and *neopentane.*

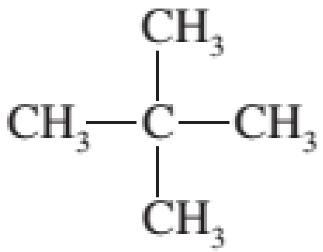
$CH_3-CH_2-CH_2-CH_2-CH_3$

pentane (*n*-pentane)



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}H-CH_2-CH_3$

isopentane



$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$

neopentane

Molecular formulas of alkenes

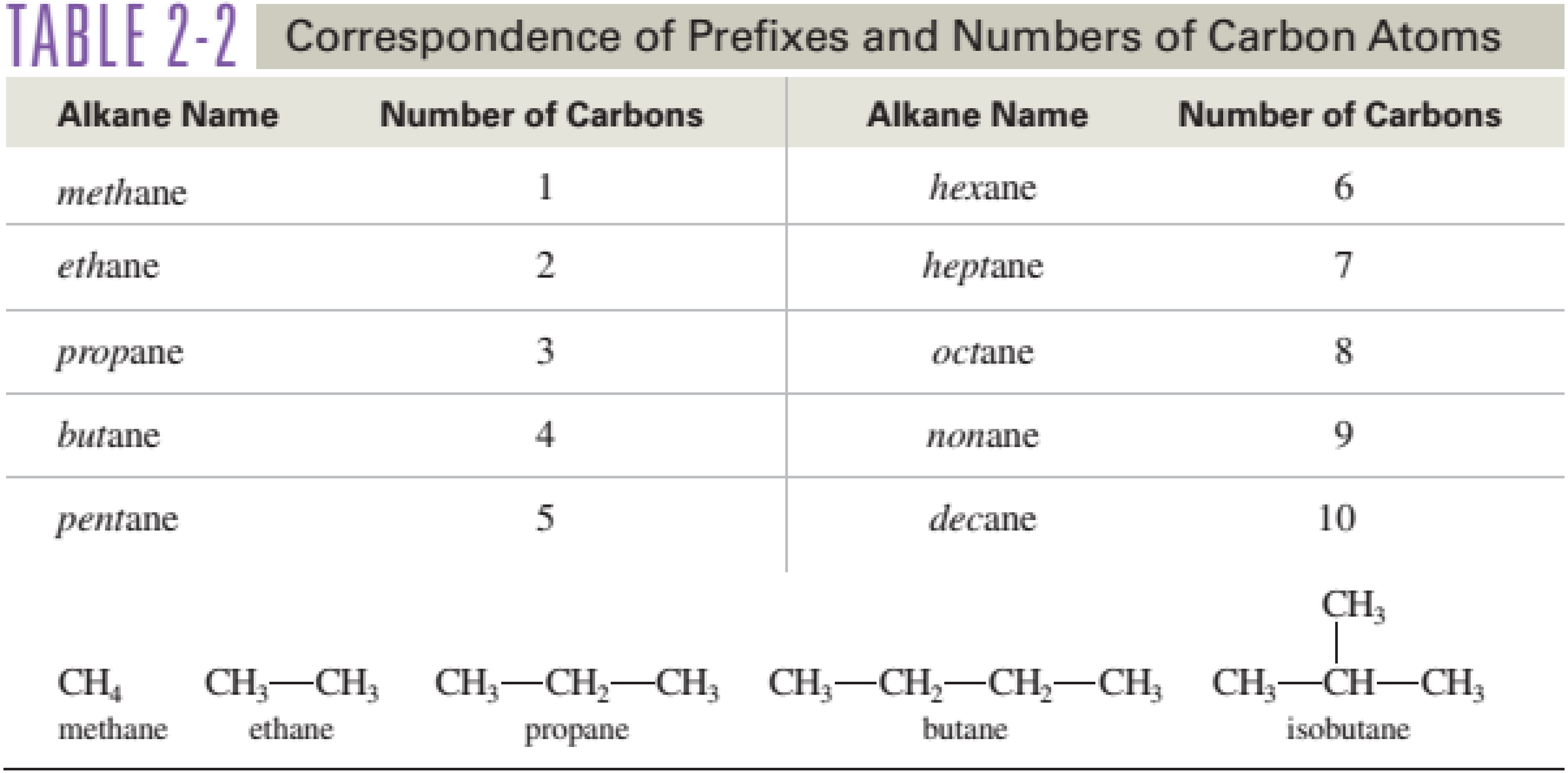


TABLE 2-2 Correspondence of Prefixes and Numbers of Carbon Atoms

Alkane Name	Number of Carbons	Alkane Name	Number of Carbons
*meth*ane	1	*hex*ane	6
*eth*ane	2	*hept*ane	7
*prop*ane	3	*oct*ane	8
*but*ane	4	*non*ane	9
*pent*ane	5	*dec*ane	10

CH_4 methane

$CH_3{-}CH_3$ ethane

$CH_3{-}CH_2{-}CH_3$ propane

$CH_3{-}CH_2{-}CH_2{-}CH_3$ butane

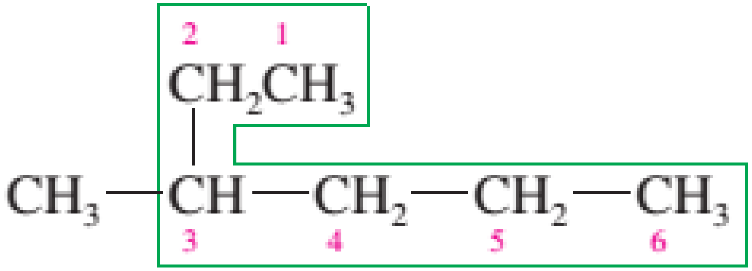
$CH_3{-}\overset{\displaystyle CH_3 \atop |}{CH}{-}CH_3$ isobutane

Nomenclature of branched alkyl groups: IUPAC or systematic names

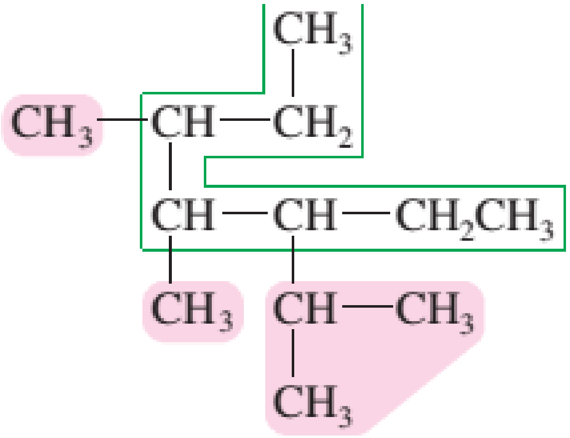
RULE 1: THE MAIN CHAIN.

- The first rule of nomenclature gives the base name of the compound.

Find the longest continuous chain of carbon atoms, and use the name of this chain as the base name of the compound.

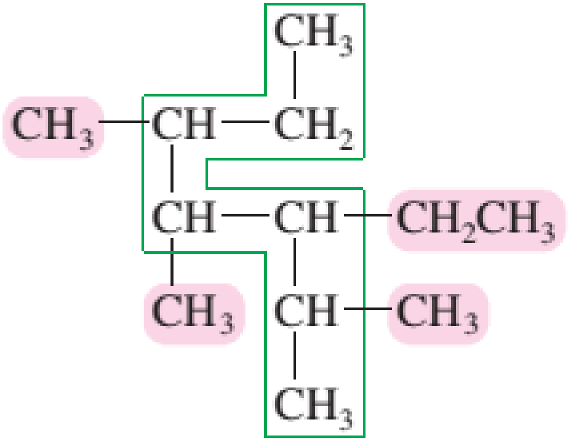


3-methyl*hexane*



wrong

seven-carbon chain, but only three substituents



correct

seven-carbon chain, four substituents

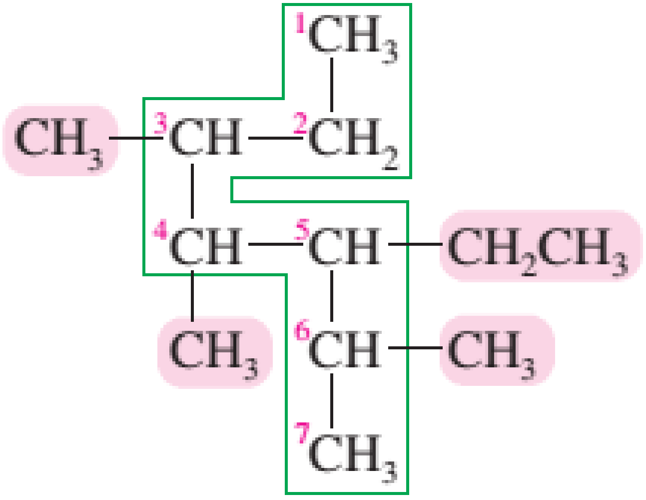
- The longest continuous chain is also called the **parent chain**.

Nomenclature of branched alkyl groups: IUPAC or systematic names

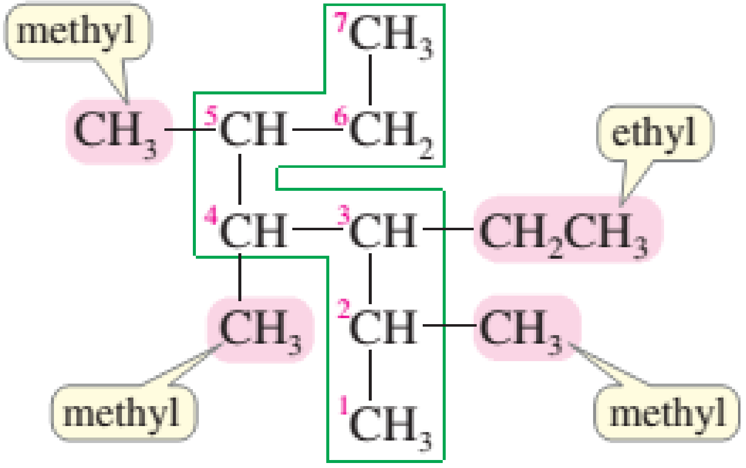
RULE 2: NUMBERING THE MAIN CHAIN

- To give the locations of the substituents, assign a number to each carbon atom on the main chain.

Number the longest chain, beginning with the end of the chain nearest a substituent.



incorrect



correct

3-ethyl-2,4,5-trimethylheptane

Nomenclature of branched alkyl groups: IUPAC or systematic names

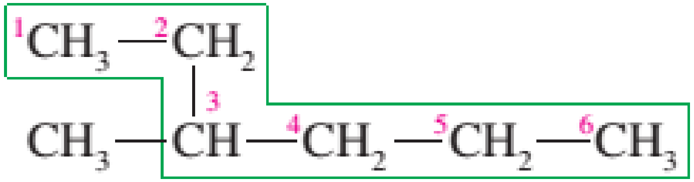
RULE 3: NAMING ALKYL GROUPS

- Name the substituent groups.

Name the substituent groups attached to the longest chain as **alkyl groups.** Give the location of each alkyl group by the number of the main-chain carbon atom to which it is attached.

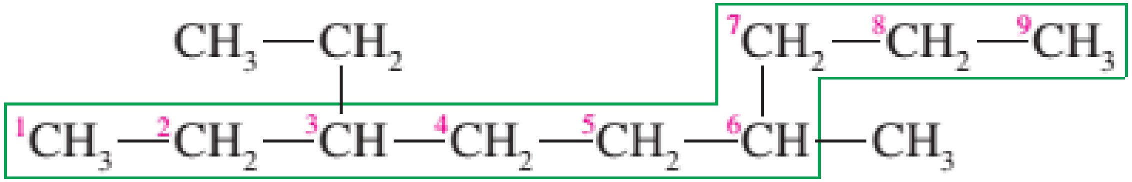
- Alkyl groups are named by replacing the -***ane*** suffix of the alkane name with –***yl***.

CH_4	methane	CH_3-	methyl group
CH_3-CH_3	ethane	CH_3-CH_2-	ethyl group
$CH_3-CH_2-CH_3$	propane	$CH_3-CH_2-CH_2-$	propyl group
$CH_3-(CH_2)_2-CH_3$	butane	$CH_3-(CH_2)_2-CH_2-$	butyl group
$CH_3-(CH_2)_3-CH_3$	pentane	$CH_3-(CH_2)_3-CH_2-$	pentyl group (*n*-amyl group)



$CH_3-\overset{\overset{{}^1CH_3-{}^2CH_2}{|}}{{}^3CH}-{}^4CH_2-{}^5CH_2-{}^6CH_3$

3-methylhexane



${}^1CH_3-{}^2CH_2-\overset{\overset{CH_3-CH_2}{|}}{{}^3CH}-{}^4CH_2-{}^5CH_2-\overset{\overset{{}^7CH_2-{}^8CH_2-{}^9CH_3}{|}}{{}^6CH}-CH_3$

3-ethyl-6-methylnonane

Nomenclature of branched alkyl groups: IUPAC or systematic names

- The *propyl* and *butyl* groups are simply unbranched three- and fourcarbon alkyl groups. These groups are sometimes named as "*n*-propyl" and "*n*-butyl".

One carbon

$CH_3—$

methyl group

Two carbons

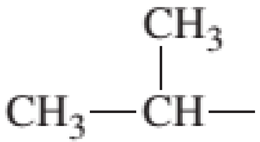
$CH_3—CH_2—$

ethyl group

Three carbons

$CH_3—CH_2—CH_2—$

propyl group
(or "*n*-propyl group")



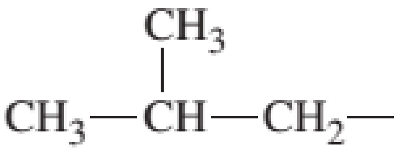
$CH_3—CH(CH_3)—$

isopropyl group

Four carbons

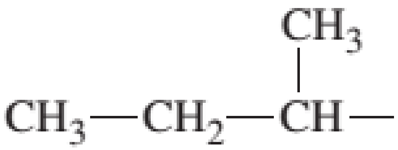
$CH_3—CH_2—CH_2—CH_2—$

butyl group
(or "*n*-butyl group")



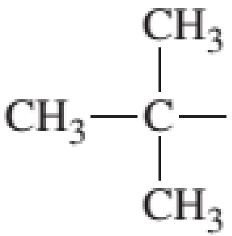
$CH_3—CH(CH_3)—CH_2—$

isobutyl group



$CH_3—CH_2—CH(CH_3)—$

sec-butyl group



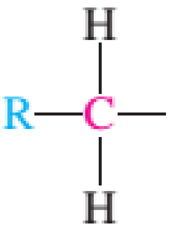
$CH_3—C(CH_3)_2—$

tert-butyl group
(or "*t*-butyl group")

Nomenclature of branched alkyl groups

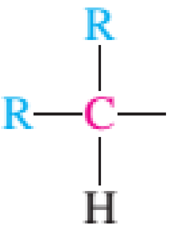
- The names of the ***secondary***-butyl (***sec***-butyl) and ***tertiary***-butyl (***tert***-butyl or *t*-butyl) groups are based on the **degree of alkyl substitution** of the carbon atom attached to the main chain.

- In the *sec*-butyl group, the carbon atom bonded to the main chain is **secondary** (2°) (or bonded to two other carbon atoms).
- In the *tert*-butyl group, it is **tertiary** (3°) (or bonded to three other carbon atoms).
- In both the *n*-butyl group and the isobutyl group, the carbon atoms bonded to the main chain are **primary** (1°), bonded to only one other carbon atom.



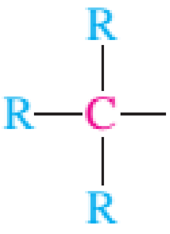
$\mathrm{R{-}\overset{H}{\underset{H}{C}}{-}}$

a *primary* (1°) carbon



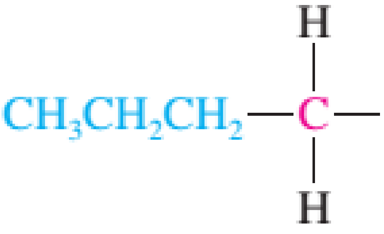
$\mathrm{R{-}\overset{R}{\underset{H}{C}}{-}}$

a *secondary* (2°) carbon



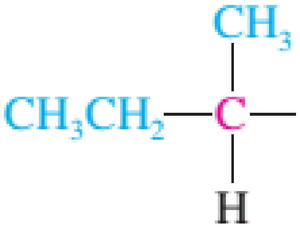
$\mathrm{R{-}\overset{R}{\underset{R}{C}}{-}}$

a *tertiary* (3°) carbon



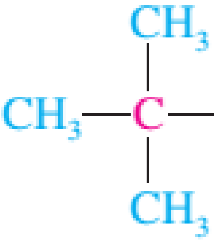
$\mathrm{CH_3CH_2CH_2{-}\overset{H}{\underset{H}{C}}{-}}$

n-butyl group (1°)



$\mathrm{CH_3CH_2{-}\overset{CH_3}{\underset{H}{C}}{-}}$

sec-butyl group (2°)



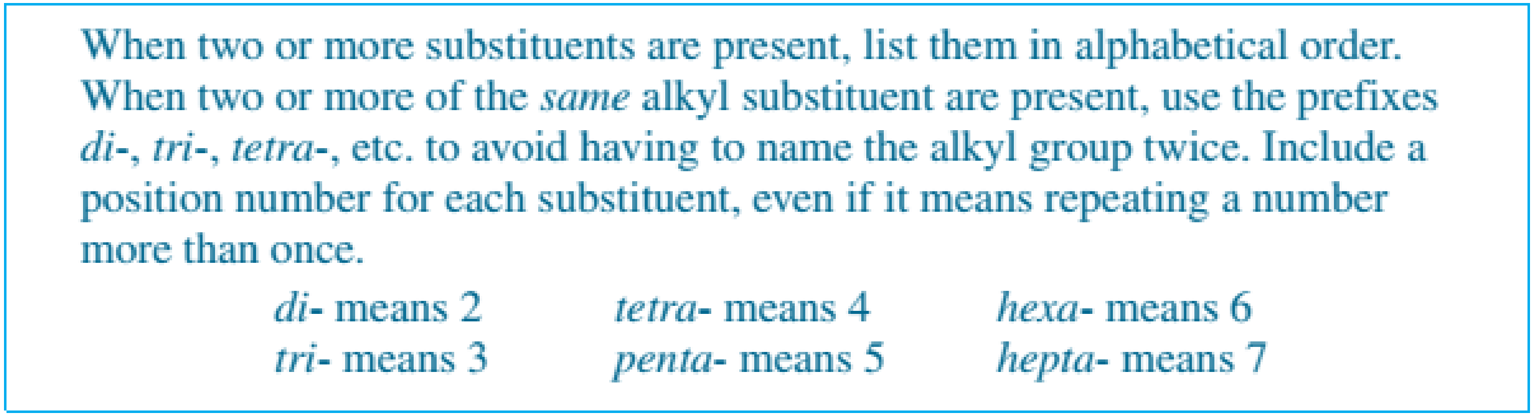
$\mathrm{CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}}$

tert-butyl group (3°)

Nomenclature of branched alkyl groups: IUPAC or systematic names

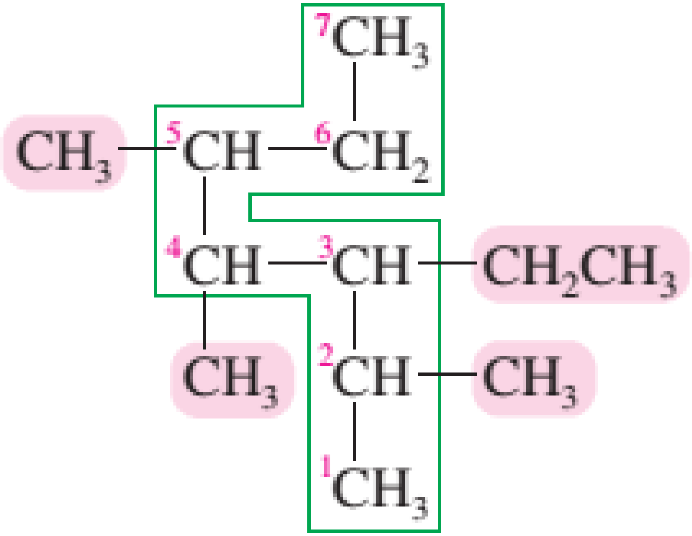
RULE 4: ORGANIZING MULTIPLE GROUPS

- The final rule deals with naming compounds with more than one substituent.



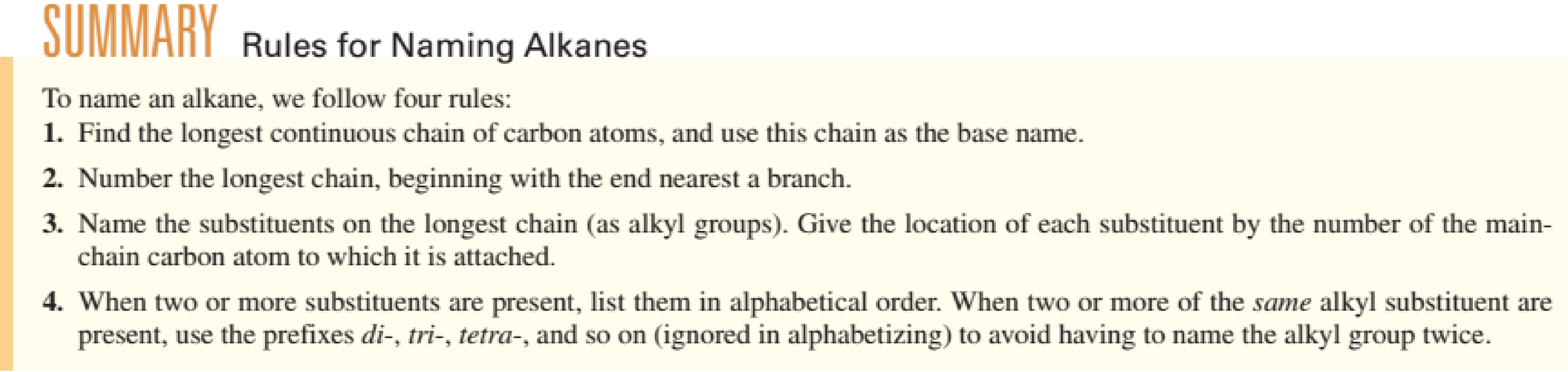
When two or more substituents are present, list them in alphabetical order. When two or more of the *same* alkyl substituent are present, use the prefixes *di*-, *tri*-, *tetra*-, etc. to avoid having to name the alkyl group twice. Include a position number for each substituent, even if it means repeating a number more than once.

di- means 2
tri- means 3
tetra- means 4
penta- means 5
hexa- means 6
hepta- means 7



3-ethyl-2,4,5-trimethylheptane

Nomenclature of branched alkyl groups: IUPAC or systematic names

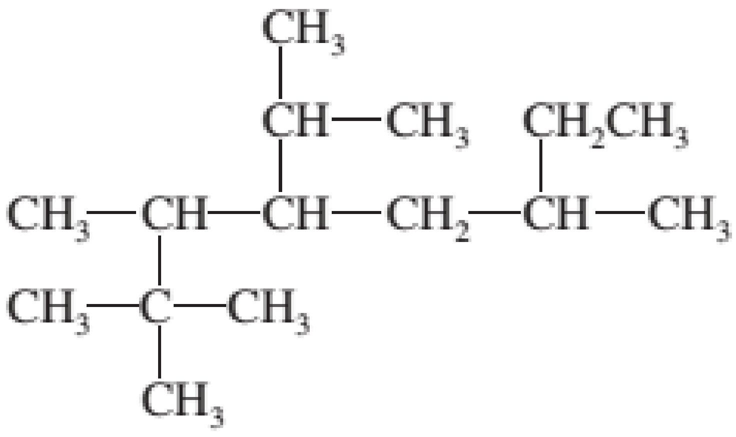


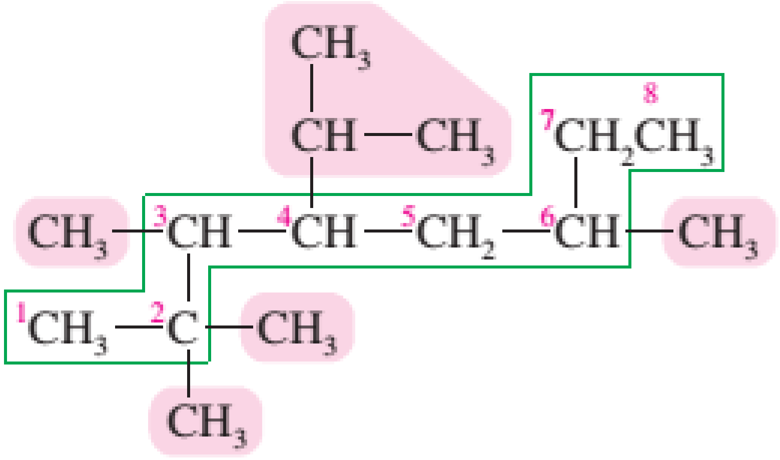
SUMMARY Rules for Naming Alkanes

To name an alkane, we follow four rules:

1. Find the longest continuous chain of carbon atoms, and use this chain as the base name.
2. Number the longest chain, beginning with the end nearest a branch.
3. Name the substituents on the longest chain (as alkyl groups). Give the location of each substituent by the number of the main-chain carbon atom to which it is attached.
4. When two or more substituents are present, list them in alphabetical order. When two or more of the *same* alkyl substituent are present, use the prefixes *di*-, *tri*-, *tetra*-, and so on (ignored in alphabetizing) to avoid having to name the alkyl group twice.

Give a systematic (IUPAC) name for the following compound.





4-Isopropyl-2,2,3,6-tetramethyloctane

Physical properties

❖ Solubilities and densities of alkanes

- Alkanes are **nonpolar**, so they dissolve in nonpolar or weakly polar organic solvents.

- Alkanes are said to be **hydrophobic** ("water hating") because they do not dissolve in water.

- Alkanes are good lubricants and preservatives for metals because they keep water from reaching the metal surface and causing corrosion.

- Alkanes have densities around **0.7 g/mL**, compared with a density of 1.0 g/mL for water.

➢ Because alkanes are less dense than water and insoluble in water, a mixture of an alkane (such as gasoline or oil) and water quickly separates into two phases, with the alkane on top.

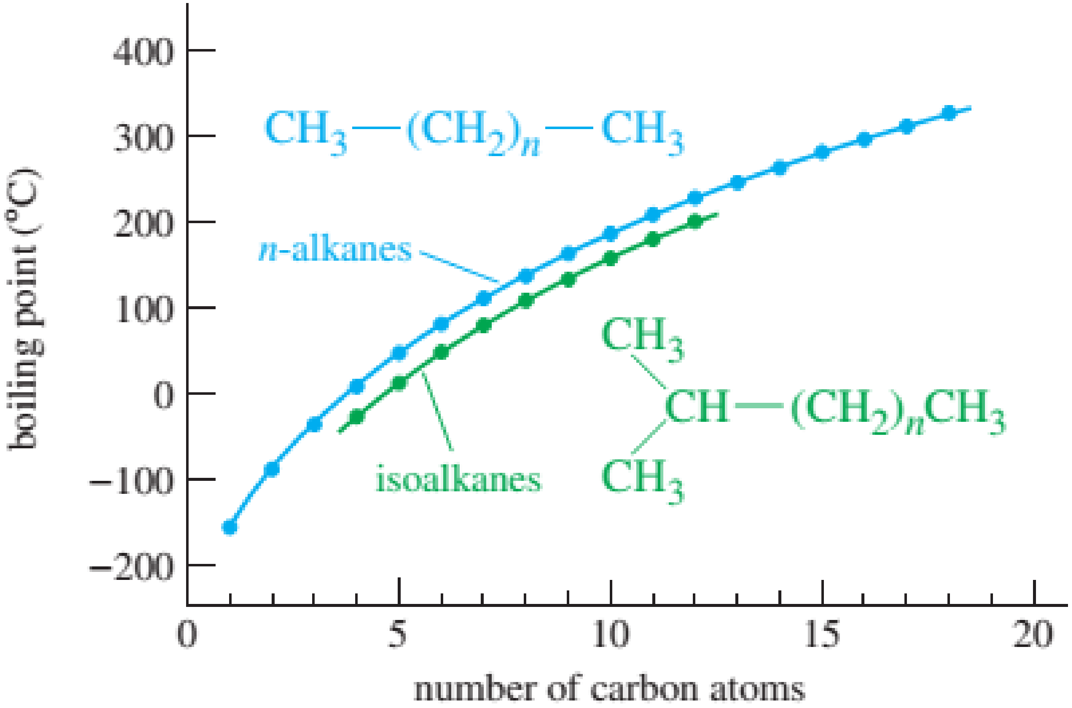
Oil floats on water. Note how the oil floats on top of the water, where it can be burned off.

Physical properties

❖ Alkane boiling points

- The graph of *n*-alkane boiling points versus the number of carbon atoms (the blue line) shows that boiling points increase with increasing molecular weight.

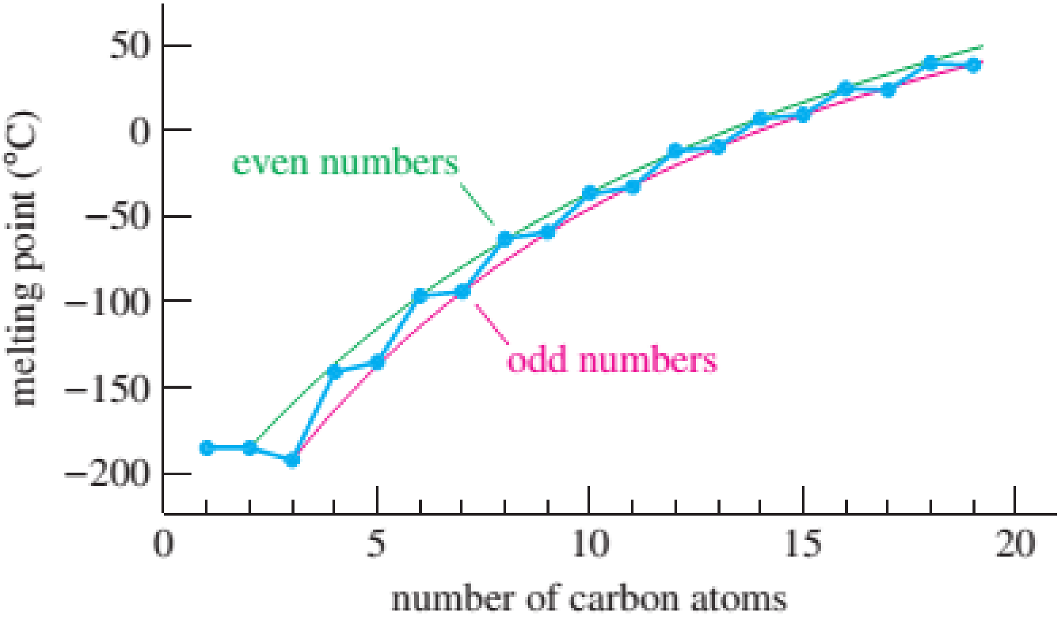
- ➢ The boiling points of the unbranched alkanes (blue) are compared with those of some branched alkanes (green).
- ➢ Because of their smaller surface areas, branched alkanes have lower boiling points than unbranched alkanes.



Physical properties

❖ Melting points of alkanes

- Like their boiling points, the melting points increase with increasing molecular weight.



The **blue** line is a graph of the melting points of the *n*-alkanes.

- ➢ Alkanes with even numbers of carbon atoms pack better into a solid structure, so that higher temperatures are needed to melt them.
- ➢ Alkanes with odd numbers of carbon atoms do not pack as well, and they melt at lower temperatures.

Chemical properties

- An **alkane** is a hydrocarbon that contains only non-polar single bonds.

- The alkanes are the simplest and least reactive class of organic compounds because they contain only hydrogen and sp^3 hybridized carbon, and they have no reactive functional groups.

+ They are poor acids and bases, and

+ They are poor electrophiles and nucleophiles as well.

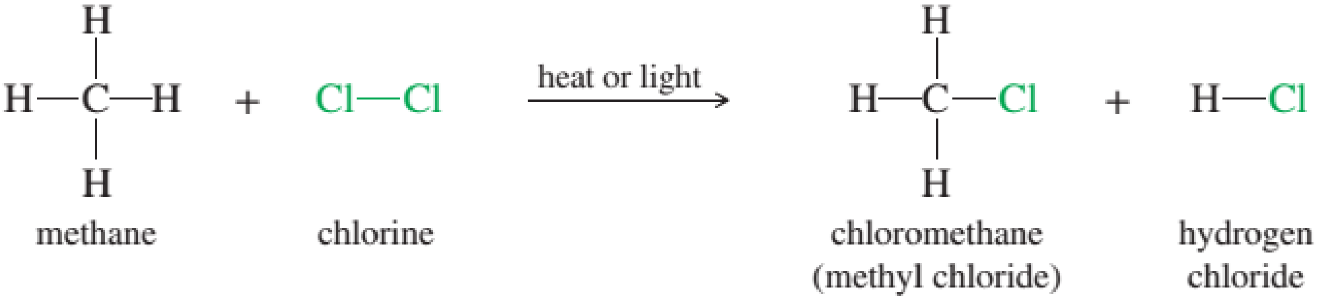
+ Although alkanes undergo reactions such as cracking and combustion at high temperatures, they are much less reactive than other classes of compounds that have functional groups.

Chemical properties: Halogenation reaction

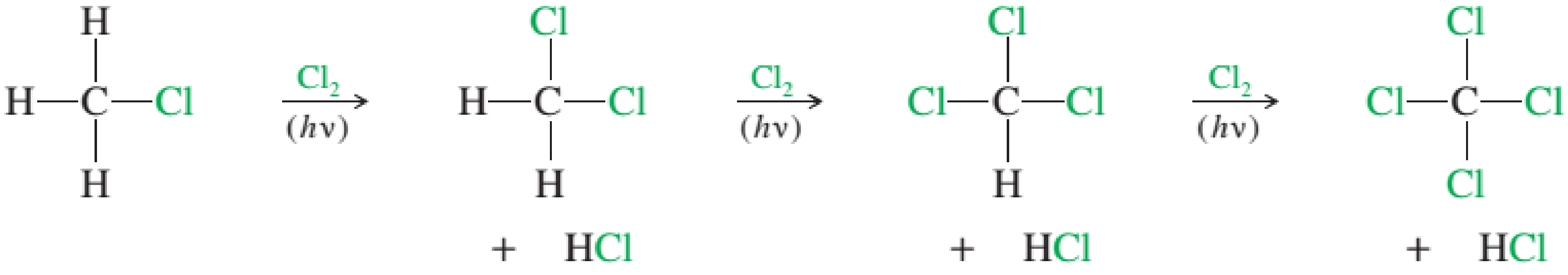
Chlorination of methane

- The chlorination of methane is an important industrial reaction.
- The reaction of methane with chlorine produces a mixture of chlorinated products, whose composition depends on the amount of chlorine added and also on the reaction conditions.
- Either light or heat is needed for the reaction to take place at a useful rate.

- When chlorine is added to methane, the first reaction is:



- This reaction may continue; heat (Δ) or light ($h\nu$) is needed for each step:



Chemical properties

- This sequence raises several questions about the chlorination of methane.

- ➢ Why is heat or light needed for the reaction to go?
- ➢ Why do we get a mixture of products?
- ➢ Is there any way to modify the reaction to get just one pure product?
- ➢ Are the observed products formed because they are the most stable products possible? Or are they favored because they are formed faster than any other products?

- A **chain reaction** mechanism has been proposed to explain the chlorination of methane. Such a reaction consists of **three** kinds of steps:

1. The **initiation step**, which generates a reactive intermediate.

2. **Propagation steps**, in which the reactive intermediate reacts with a stable molecule to form a product and another reactive intermediate, allowing the chain to continue.

3. **Termination steps**, side reactions that destroy reactive intermediates and tend to slow or stop the reaction.

Chlorination: A chain reaction

1. The initiation step - Generation of a reactive intermediate - Radicals

- Blue light, absorbed by chlorine but not by methane, promotes this reaction. Blue light has about the right energy to split a chlorine molecule into two chlorine atoms, which requires 242 kJ mol (58 kcal mol).

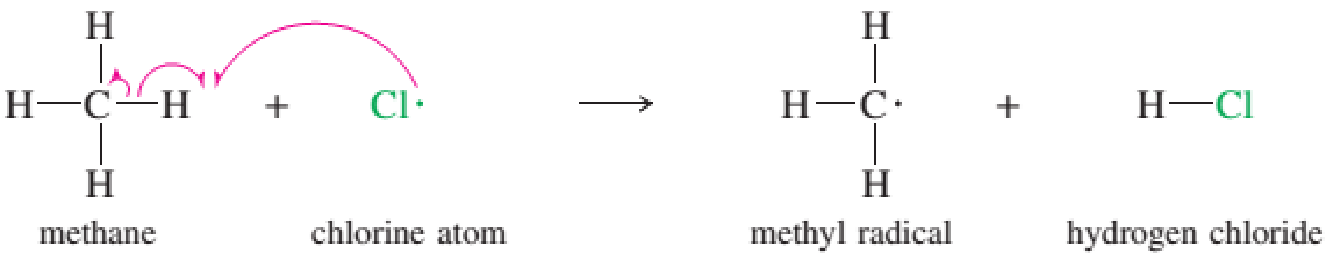
- Notice the fishhook-shaped half-arrows used to show the movement of single unpaired electrons.
- The splitting of a molecule is an initiation step that produces two highly reactive chlorine atoms.
- A chlorine atom is an example of a **reactive intermediate**, a short-lived species that is never present in high concentration because it reacts as quickly as it is formed. Each has an odd number of valence electrons (seven), one of which is unpaired.
- Species with unpaired electrons are called **radicals** or **free radicals**. Radicals are electron-deficient because they lack an octet. The odd electron readily combines with an electron in another atom to complete an octet and form a bond.

Chlorination: A chain reaction

2. Propagation steps - Formation of products with regeneration of reactive intermediates.

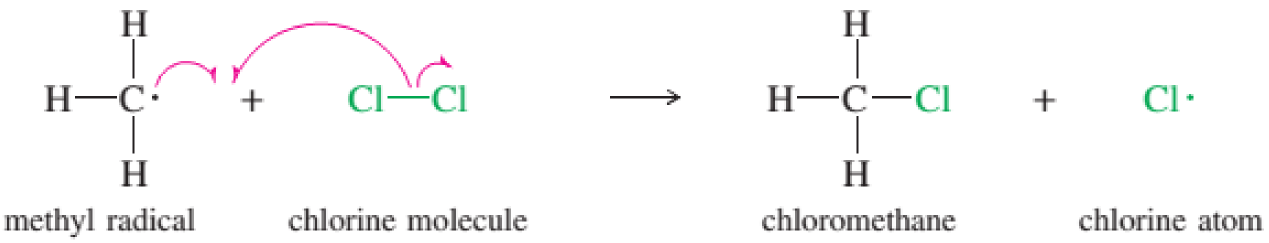
- When a chlorine radical collides with a methane molecule, it abstracts (removes) a hydrogen atom from methane. One of the electrons in the bond remains on carbon while the other combines with the odd electron on the chlorine atom to form the H-Cl bond.

First propagation step



- Notice that the first propagation step begins with one free radical (**the chlorine atom**) and produces another free radical (**the methyl radical**). The regeneration of a free radical is characteristic of a propagation step of a chain reaction.

Second propagation step

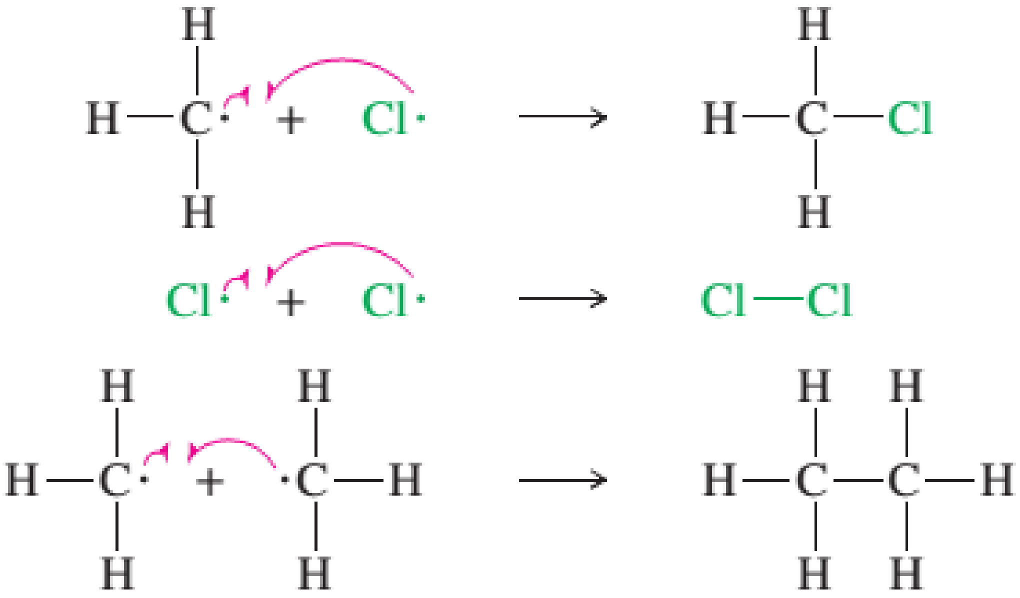


- In addition to forming chloromethane, the second propagation step produces another chlorine radical.

Chlorination: A chain reaction

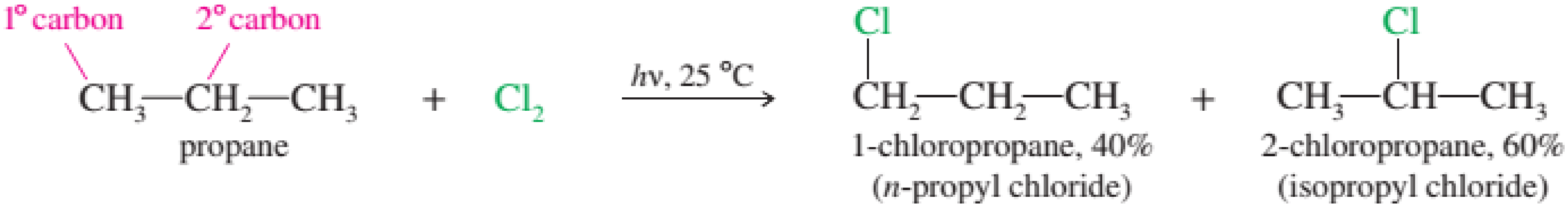
3. Termination reactions - Destruction of reactive intermediates

- If anything happens to consume some of the free-radical intermediates without generating new ones, the chain reaction will slow or stop.
- Such a side reaction is called a **termination reaction:** a step that produces fewer reactive intermediates (free radicals) than it consumes.



- The combination of any two free radicals is a termination step because it decreases the number of free radicals, finally resulting in the breaking of the chain.

Chlorination of propane: Product ratios



$$CH_3{-}CH_2{-}CH_3 + Cl_2 \xrightarrow{h\nu,\ 25\ ^\circ C} \overset{Cl}{CH_2}{-}CH_2{-}CH_3 + CH_3{-}\overset{Cl}{CH}{-}CH_3$$

propane

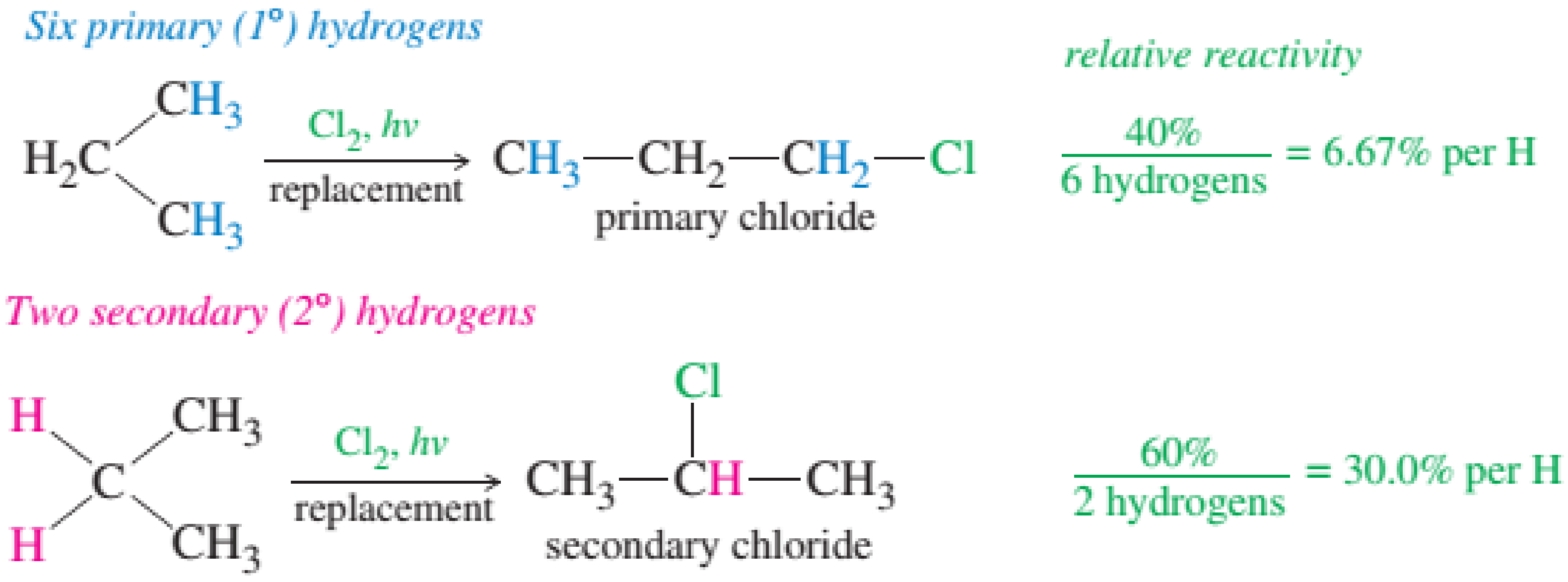
1-chloropropane, 40%
(*n*-propyl chloride)

2-chloropropane, 60%
(isopropyl chloride)

- ➢ In methane, all four hydrogen atoms are identical, and it does not matter which hydrogen is replaced.
- ➢ In the higher alkanes, replacement of different hydrogen atoms may lead to different products.
- ➢ In the chlorination of propane, for example, two monochlorinated (just one chlorine atom) products are possible. One has the chlorine atom on a primary carbon atom, and the other has the chlorine atom on the secondary carbon atom.

Chlorination of propane: Product ratios

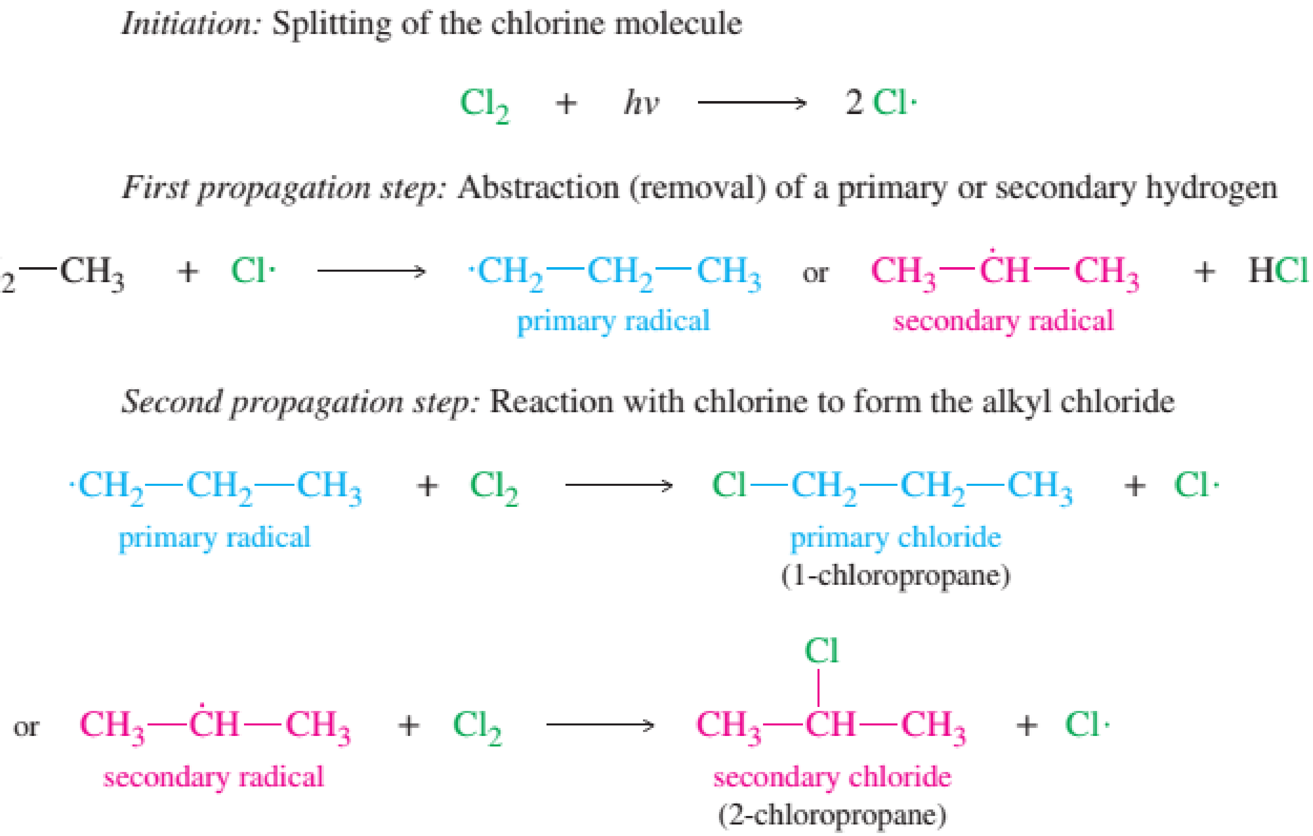
- The product ratio shows that replacement of hydrogen atoms by chlorine is not random. Propane has six primary hydrogens (hydrogens bonded to primary carbons) and only two secondary hydrogens (bonded to the secondary carbon), yet the major product results from substitution of a secondary hydrogen.
- We can calculate how reactive each kind of hydrogen is by dividing the amount of product observed by the number of hydrogens that can be replaced to give that product.



The 2° hydrogens are $\frac{30.0}{6.67} = 4.5$ times as reactive as the 1° hydrogens.

Chlorination of propane: free-radical reaction mechanism

- ➢ When a chlorine atom reacts with propane, abstraction of a hydrogen atom can give either a primary radical or a secondary radical. The structure of the radical formed in this step determines the structure of the observed product, either 1-chloropropane or 2-chloropropane.
- ➢ The product ratio shows that the secondary radical is formed preferentially. This preference for reaction at the secondary position results from the greater stability of the secondary free radical and the transition state leading to it.



Initiation: Splitting of the chlorine molecule

$$Cl_2 + h\nu \longrightarrow 2\,Cl\cdot$$

First propagation step: Abstraction (removal) of a primary or secondary hydrogen

$$CH_3{-}CH_2{-}CH_3 + Cl\cdot \longrightarrow \underset{\text{primary radical}}{\cdot CH_2{-}CH_2{-}CH_3} \text{ or } \underset{\text{secondary radical}}{CH_3{-}\dot{C}H{-}CH_3} + HCl$$

Second propagation step: Reaction with chlorine to form the alkyl chloride

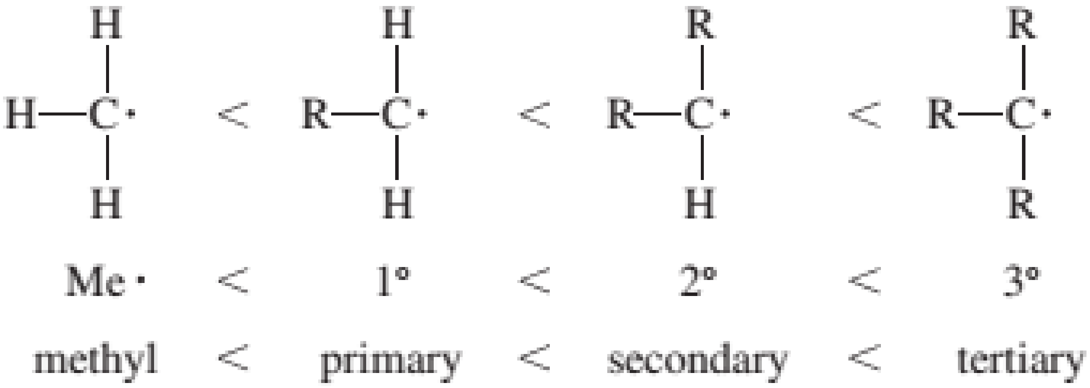
$$\underset{\text{primary radical}}{\cdot CH_2{-}CH_2{-}CH_3} + Cl_2 \longrightarrow \underset{\substack{\text{primary chloride}\\ \text{(1-chloropropane)}}}{Cl{-}CH_2{-}CH_2{-}CH_3} + Cl\cdot$$

$$\text{or } \underset{\text{secondary radical}}{CH_3{-}\dot{C}H{-}CH_3} + Cl_2 \longrightarrow \underset{\substack{\text{secondary chloride}\\ \text{(2-chloropropane)}}}{CH_3{-}\overset{\overset{\large Cl}{|}}{C}H{-}CH_3} + Cl\cdot$$

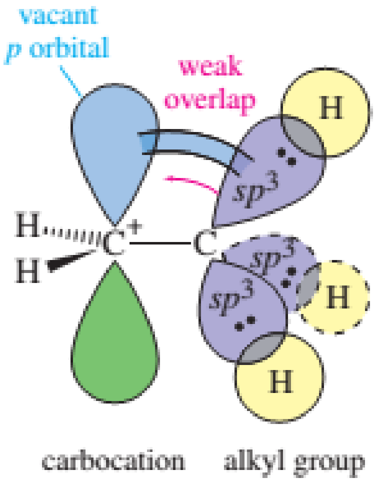
Free-radical stabilities

- Free radicals are more stable if they are more highly substituted.

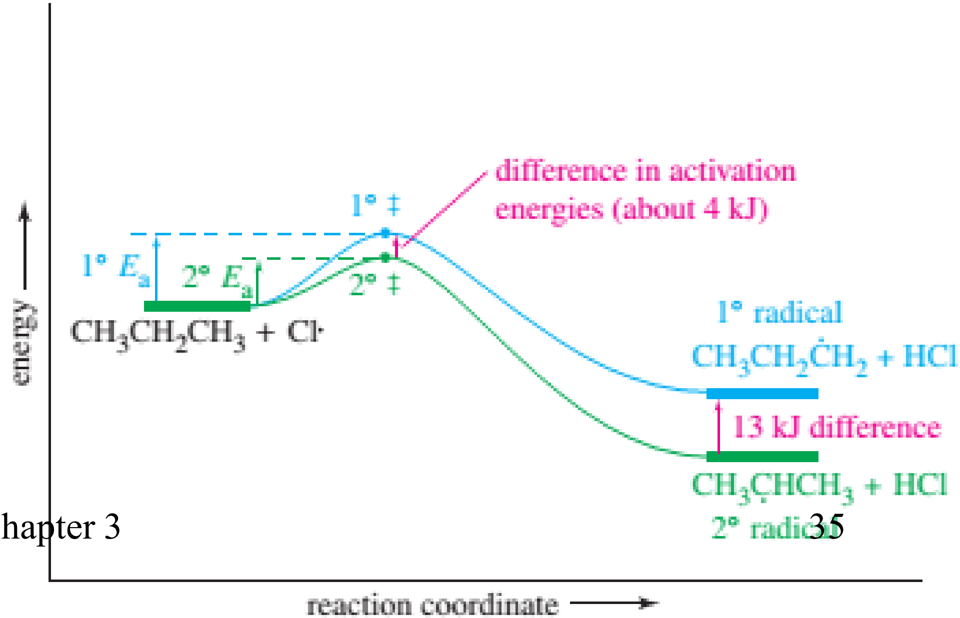
- The following free radicals are listed in increasing order of stability.

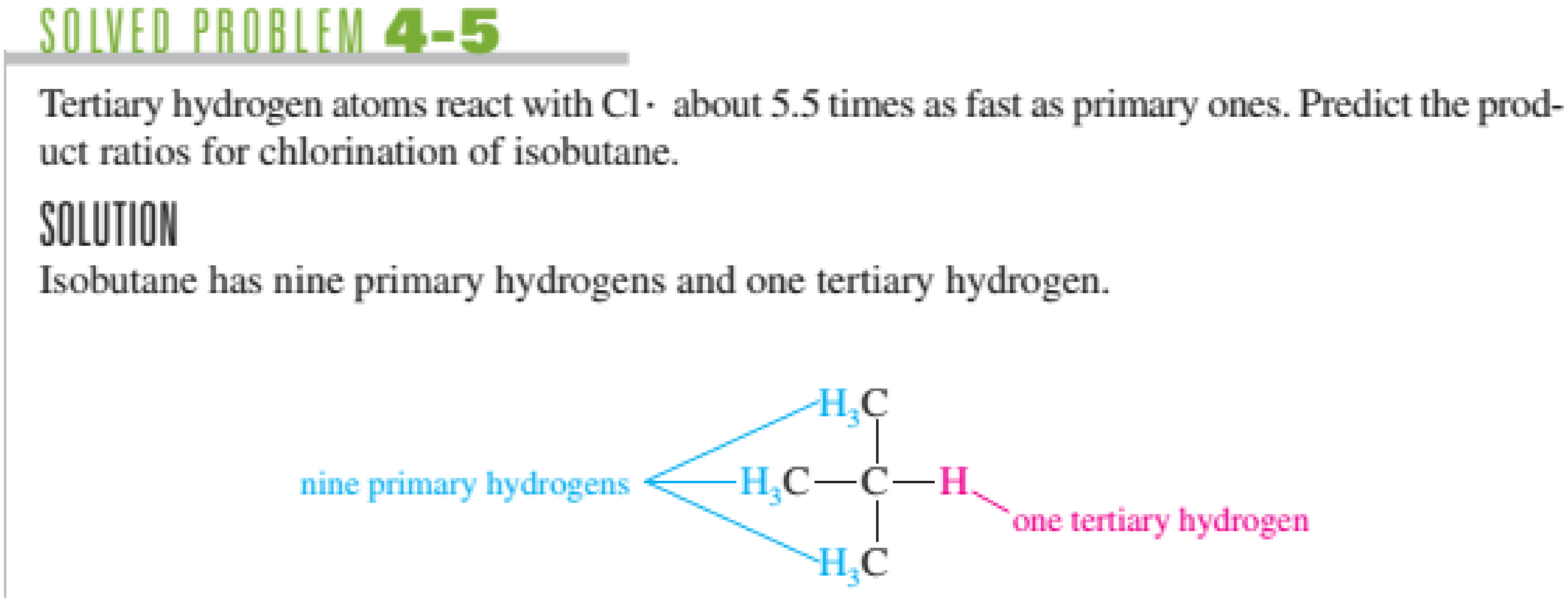


$$H_3C\cdot < RCH_2\cdot < R_2CH\cdot < R_3C\cdot$$



Reaction-energy diagram for the first propagation step in the chlorination of propane. Formation of the secondary radical has a lower activation energy than does formation of the primary radical.





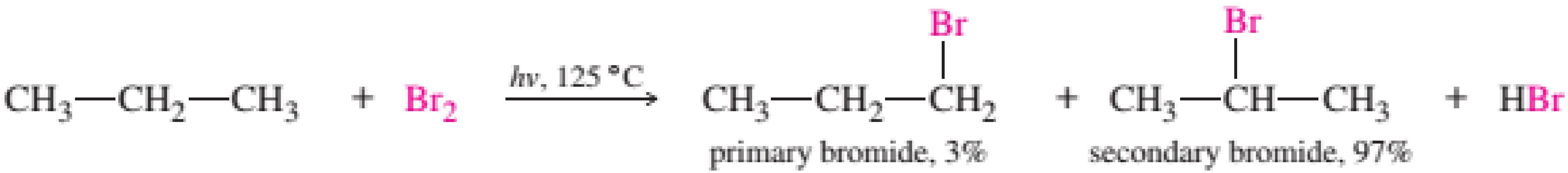
SOLVED PROBLEM 4-5

Tertiary hydrogen atoms react with Cl· about 5.5 times as fast as primary ones. Predict the product ratios for chlorination of isobutane.

SOLUTION

Isobutane has nine primary hydrogens and one tertiary hydrogen.

Bromination of Propane: more selective halogenation



$$\mathrm{CH_3{-}CH_2{-}CH_3} + \mathrm{Br_2} \xrightarrow{h\nu,\ 125\,°\mathrm{C}} \mathrm{CH_3{-}CH_2{-}}\overset{\overset{\mathrm{Br}}{|}}{\mathrm{CH_2}} + \mathrm{CH_3{-}}\overset{\overset{\mathrm{Br}}{|}}{\mathrm{CH}}\mathrm{{-}CH_3} + \mathrm{HBr}$$

primary bromide, 3%

secondary bromide, 97%

- Notice that this reaction is both heated to 125 °C and irradiated with light to achieve a moderate rate.

Relative reactivity

six primary hydrogens $\frac{3\%}{6} = 0.5\%$ per H

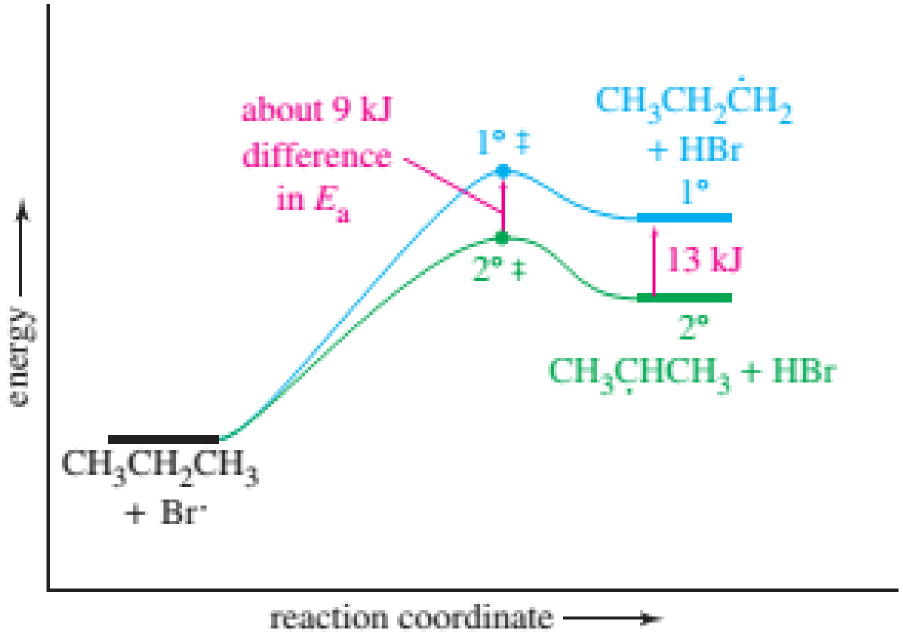
two secondary hydrogens $\frac{97\%}{2} = 48.5\%$ per H

The 2° hydrogens are $\frac{48.5}{0.5} = 97$ times as reactive as the 1° hydrogens.

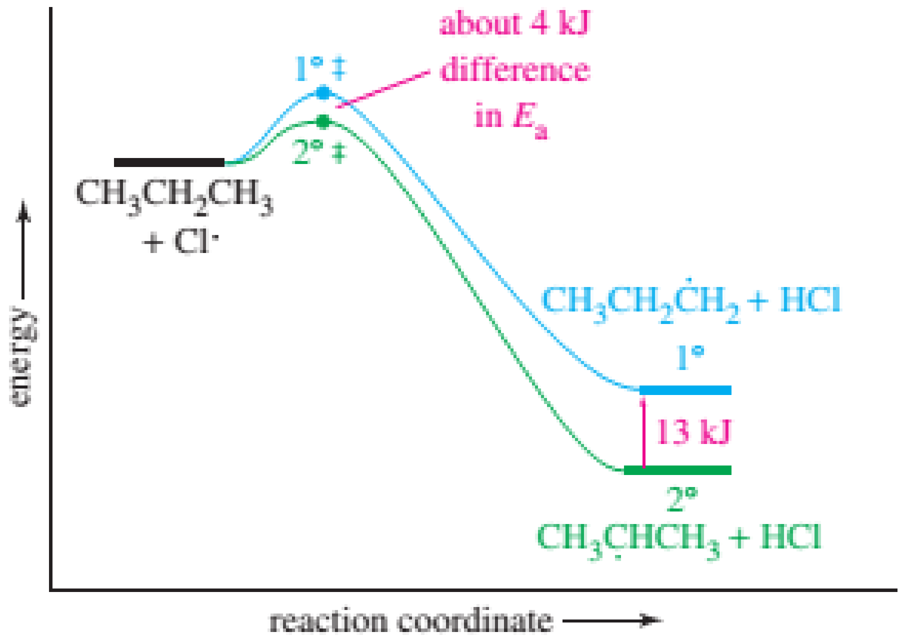
- The 97:1 reactivity ratio for bromination is much larger than the 4.5:1 ratio for chlorination. We say that bromination is **more *selective*** than chlorination because the major reaction is favored by a larger amount.

Bromination of Propane: more selective halogenation

In an endothermic reaction, the transition state is closer to the products in energy and in structure. In an exothermic reaction, the transition state is closer to the reactants in energy and in structure.

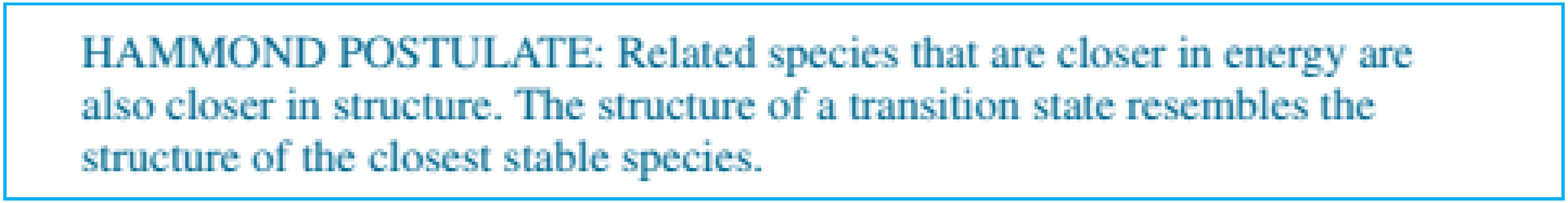


(a) BROMINATION endothermic TS close to products - **large** difference in E_a.



(b) CHLORINATION exothermic TS close to reactants - **small** difference in E_a

Hammond postulate



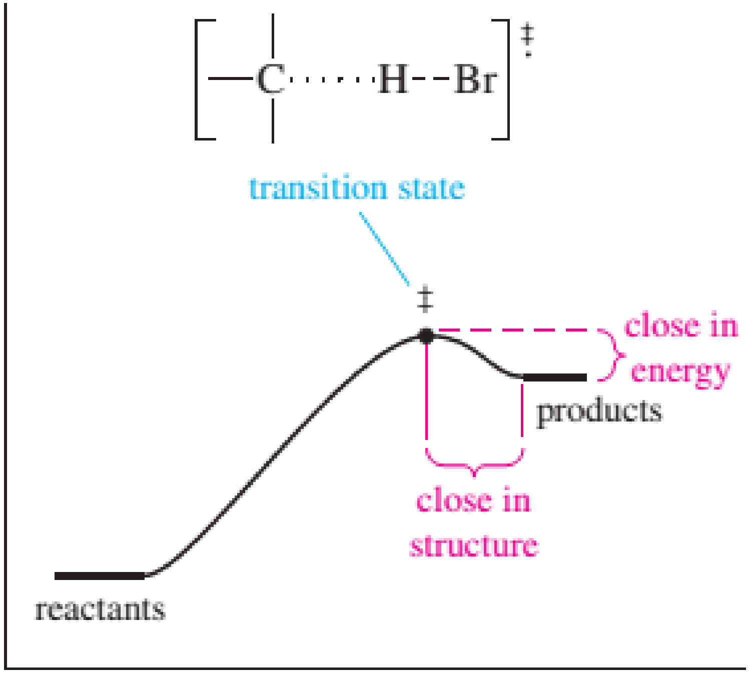
HAMMOND POSTULATE: Related species that are closer in energy are also closer in structure. The structure of a transition state resembles the structure of the closest stable species.

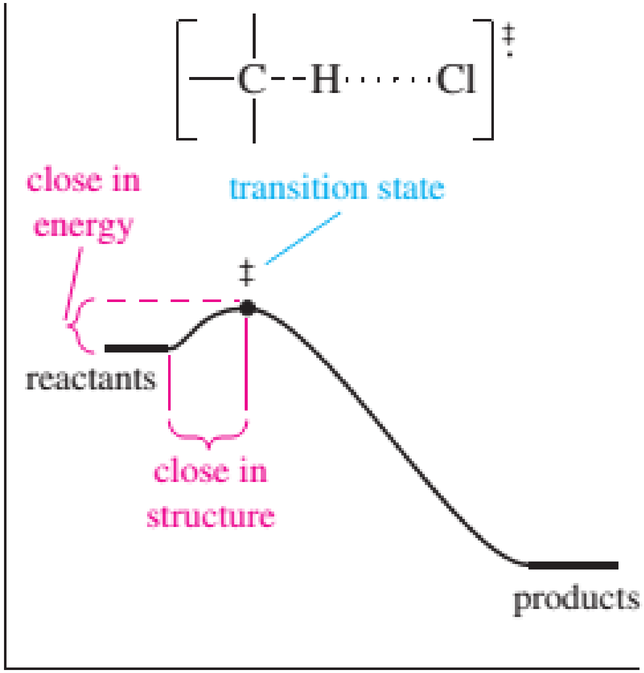
- This general rule tells us something about the transition states in endothermic and exothermic reactions. The transition state is always the point of highest energy on the energy diagram. Its structure resembles either the reactants or the products, whichever ones are higher in energy.

➢ In an endothermic reaction, the products are higher in energy, and the transition state is product-like.

➢ In an exothermic reaction, the reactants are higher in energy, and the transition state is reactant-like.

- Thus, the Hammond postulate helps us understand why exothermic processes tend to be less selective than similar endothermic processes.


[—C····H--Br]‡
transition state
‡
close in energy
products
close in structure
reactants


[—C--H····Cl]‡
close in energy
transition state
‡
reactants
close in structure
products

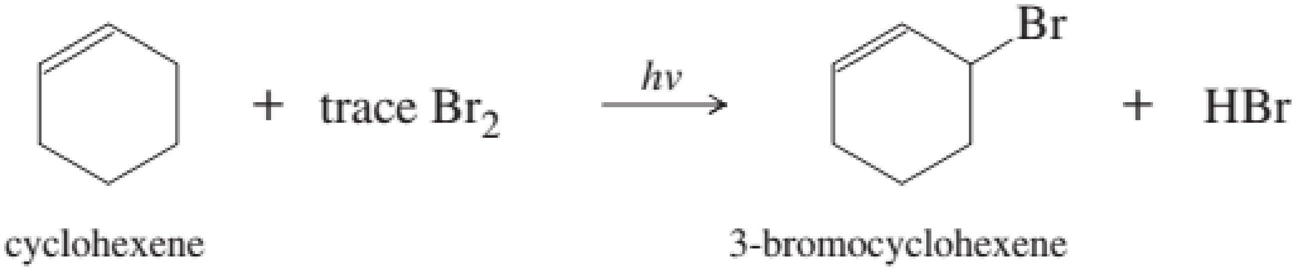
Bromination of alkanes: more selective halogenation

Problem 1

2,3-Dimethylbutane reacts with bromine in the presence of light to give a monobrominated product. Further reaction gives a good yield of a dibrominated product. Predict the structures of these products, and propose a mechanism for the formation of the monobrominated product.

Problem 2

In the presence of a small amount of bromine, cyclohexene undergoes the following light-promoted reaction:



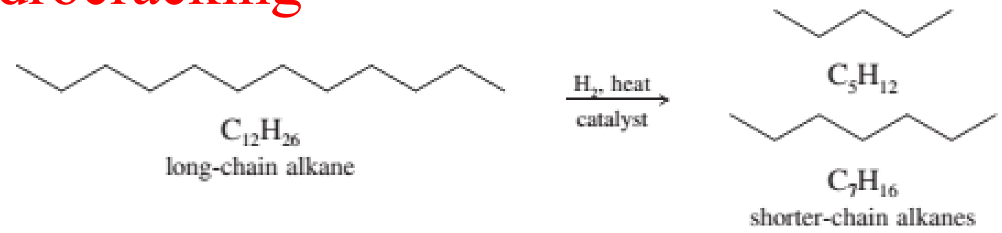
(a) Propose a mechanism for this reaction.
(b) Draw the structure of the rate-limiting transition state.

Other reactions of alkanes

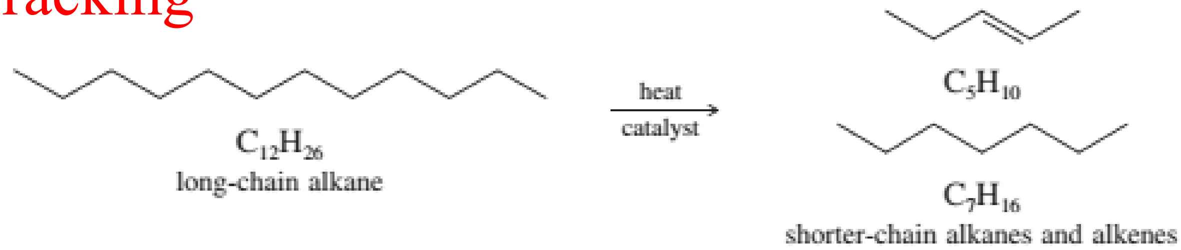
- ❖ Combustion

$$C_nH_{(2n+2)} + \text{excess } O_2 \xrightarrow{\text{heat}} n\,CO_2 + (n+1)\,H_2O$$

- ❖ Catalytic hydrocracking

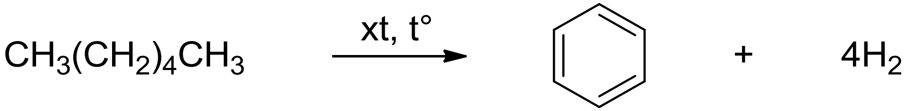


- ❖ Catalytic cracking



- ❖ Metal-catalyzed dehydrogenation of alkanes

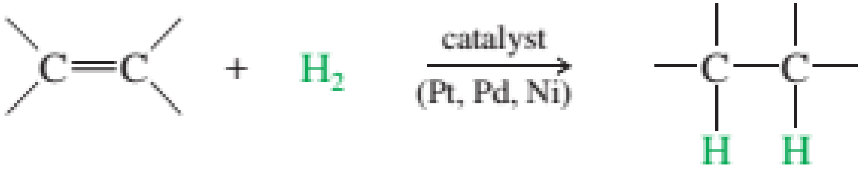
$$CH_3\text{-}CH_2CH_2\text{-}CH_3 \xrightleftharpoons{\text{Pt, t°}} CH_3CH{=}CHCH_3 + H_2$$



Alkane synthesis: In laboratory

❖ Catalytic hydrogenation of alkenes

- Hydrogenation of an alkene is formally a reduction, with adding across the double bond to give an alkane. The process usually requires a catalyst containing Pt, Pd, or Ni.



Example

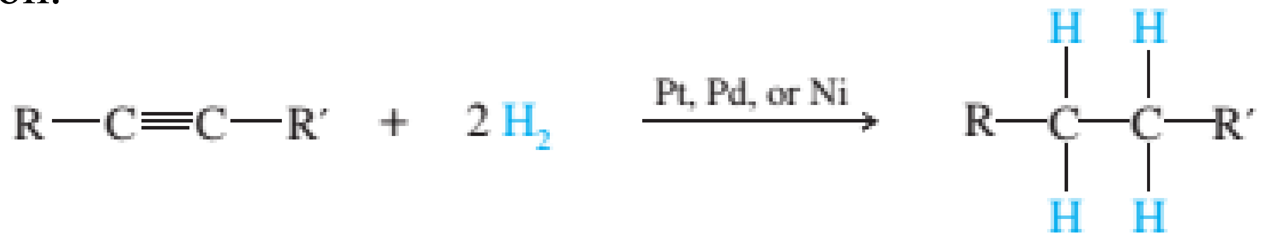
$$CH_3{-}CH{=}CH{-}CH_3 \quad + \quad H_2 \quad \xrightarrow{Pt} \quad CH_3{-}CH_2{-}CH_2{-}CH_3$$

- For most alkenes, hydrogenation takes place at room temperature, using hydrogen gas at atmospheric pressure. The alkene is usually dissolved in an alcohol, an alkane, or acetic acid. A small amount of platinum, palladium, or nickel catalyst is added, and the container is shaken or stirred while the reaction proceeds.

Laboratory alkane synthesis

❖ Catalytic hydrogenation of alkynes

- ➢ In the presence of a suitable catalyst, hydrogen adds to an alkyne, reducing it to an alkane. Platinum, palladium, and nickel catalysts are commonly used in this reduction.



$$R-C\equiv C-R' + 2\,H_2 \xrightarrow{\text{Pt, Pd, or Ni}} R-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-\overset{\overset{\large H}{|}}{\underset{\underset{\large H}{|}}{C}}-R'$$

- ➢ When either of the butyne isomers reacts with hydrogen and a platinum catalyst, the product is *n*-butane.

Examples

$$\underset{\text{but-1-yne}}{H-C\equiv C-CH_2CH_3} + 2\,H_2 \xrightarrow{Pt} \underset{\substack{\text{butane}\\(100\%)}}{H-CH_2-CH_2-CH_2CH_3}$$

$$\underset{\text{but-2-yne}}{CH_3-C\equiv C-CH_3} + 2\,H_2 \xrightarrow{Pt} \underset{\substack{\text{butane}\\(100\%)}}{CH_3-CH_2-CH_2-CH_3}$$

Laboratory alkane synthesis

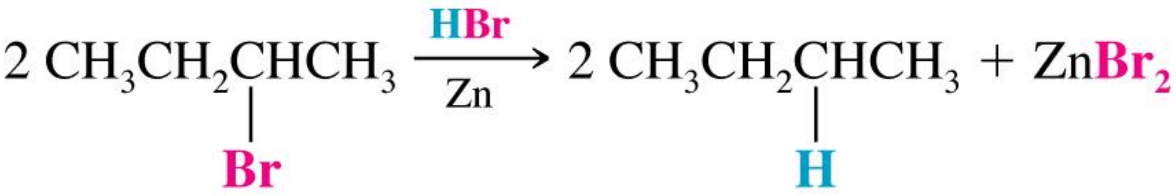
❖ Reduction of alkyl halides

$$R{-}X + Zn + HX \longrightarrow R{-}H + ZnX_2$$

or*

$$R{-}X \xrightarrow[(-ZnX_2)]{Zn,\ HX} R{-}H$$

- Example



$$2\ CH_3CH_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow[Zn]{HBr} 2\ CH_3CH_2\underset{\displaystyle H}{\underset{|}{C}}HCH_3 + ZnBr_2$$

***sec*-Butyl bromide**
(2-bromobutane)

Butane

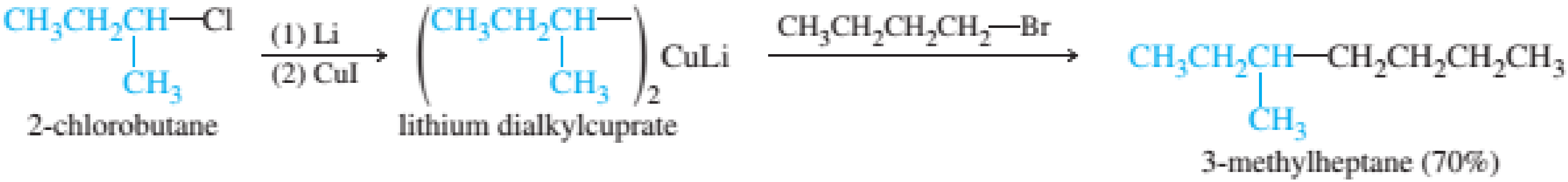
Laboratory alkane synthesis – Corey – House synthesis

- ❖ Cross-coupling of alkyl halide and lithium dialkylcuprate

$$R_2CuLi \quad + \quad R'{-}X \longrightarrow R{-}R' \quad + \quad R{-}Cu \quad + \quad LiX$$

a lithium dialkylcuprate

Example



$$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}Cl \xrightarrow[(2)\ CuI]{(1)\ Li} \left(CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}\right)_2 CuLi \xrightarrow{CH_3CH_2CH_2CH_2{-}Br} CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2CH_2CH_2CH_3$$

Laboratory alkane synthesis – Corey – House synthesis

- Reduction of alkyl halide *via* hydrolysis of organometalic reagents

$$R{-}X + Mg \xrightarrow[\text{ether}]{} R{-}MgX \xrightarrow{H_2O} R{-}H + XMgOH$$

$$R{-}X + 2\,Li \longrightarrow R{-}Li + LiX \xrightarrow{H_2O} R{-}H + LiOH$$

Uses and sources of alkanes

C1–C2 Methane and ethane are gases at room temperature and atmospheric pressure. They are difficult to liquefy, so they are usually handled as compressed gases. Upon cooling to cryogenic (very low) temperatures, however, methane and ethane become liquids. *Liquefied natural gas*, mostly methane, can be transported in special refrigerated tankers more easily than it can be transported as a compressed gas.

C3–C4 Propane and butane are also gases at room temperature and pressure, but they are easily liquefied at room temperature under modest pressure. These gases, often obtained along with liquid petroleum, are stored in low-pressure cylinders of *liquefied petroleum gas (LPG)*. Propane and butane are good fuels, both for heating and for internal combustion engines. They burn cleanly, and pollution-control equipment is rarely necessary. In many agricultural areas, propane and butane are more cost-effective tractor fuels than gasoline and diesel fuel. Propane and butane have largely replaced Freons® (see Section 6-3D) as propellants in aerosol cans. Unlike alkanes, the chlorofluorocarbon Freon propellants are implicated in damaging the earth's protective ozone layer.

Clean-burning propane-powered vehicles help to reduce air pollution in urban areas

Uses and sources of alkanes

C5–C8 The next four alkanes are free-flowing, volatile liquids. Isomers of pentane, hexane, heptane, and octane are the primary constituents of gasoline. Their volatility is crucial for this use because the injection system simply squirts a stream of gasoline into the intake air as it rushes through. If gasoline did not evaporate easily, it would reach the cylinder in the form of droplets. Droplets cannot burn as efficiently as a vapor, so the engine would smoke and give low mileage.

C9–C16 The nonanes through about the hexadecanes are higher-boiling liquids that are somewhat viscous. These alkanes are used in kerosene, jet fuel, and diesel fuel. **Kerosene,** the lowest-boiling of these fuels, was once widely available but is now harder to find. It is less volatile than gasoline and less prone to forming explosive mixtures. Kerosene was used in kerosene lamps and heaters, which use wicks to allow this heavier fuel to burn. Jet fuel is similar to kerosene, but more highly refined and less odorous.

C16 and Up Alkanes with more than 16 carbon atoms are most often used as lubricating and heating oils. These are sometimes called “mineral” oils because they come from petroleum, which was once considered a mineral. Paraffin “wax” is not a true wax, but a purified mixture of high-molecular- eight alkanes with melting points well above room temperature.

Alkane sources - Petroleum refining

- Alkanes are derived mostly from petroleum and petroleum by-products. *Petroleum*, often called *crude oil*, is pumped from wells that reach into pockets containing the remains of prehistoric plants. The principal constituents of crude oil are alkanes, some aromatics, and some undesirable compounds containing sulfur and nitrogen.
- The first step in refining petroleum is a careful fractional distillation. The products of that distillation are not pure alkanes but mixtures of alkanes with useful ranges of boiling points. Table below shows the major fractions obtained from the distillation of crude petroleum.

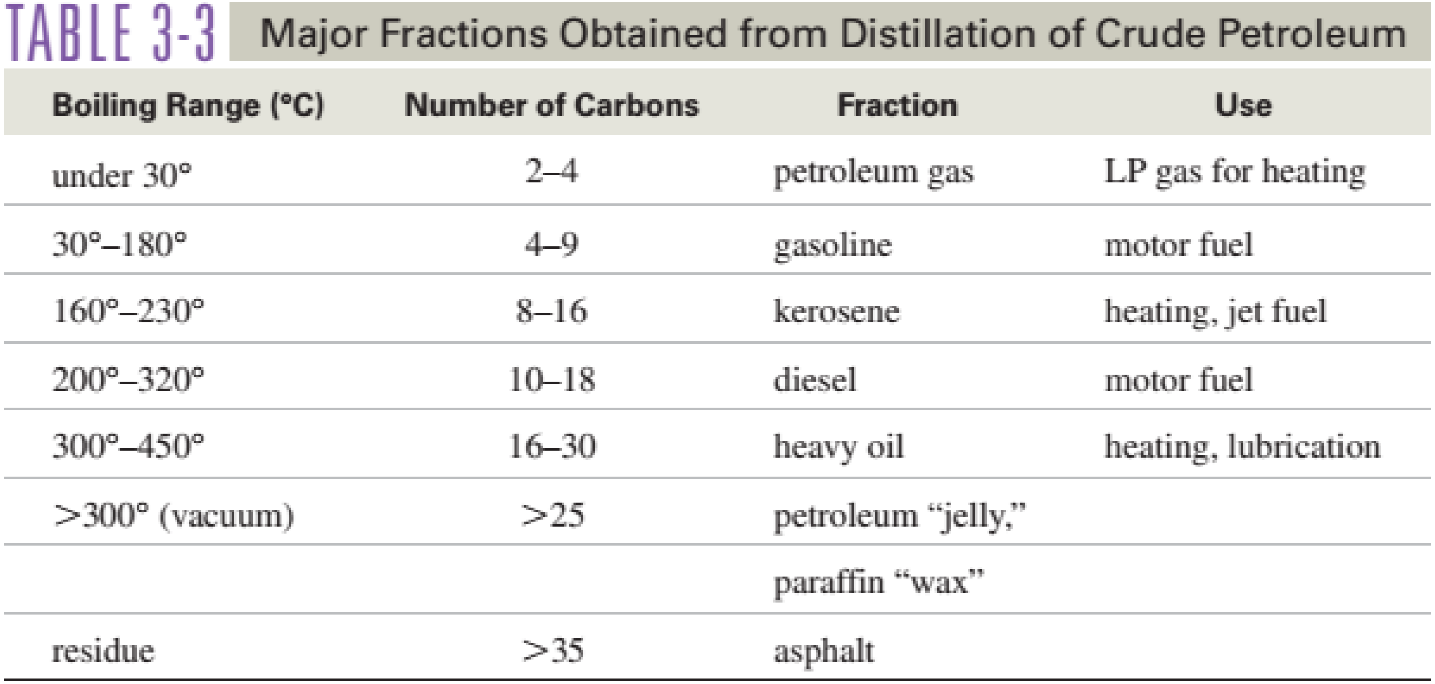


TABLE 3-3 Major Fractions Obtained from Distillation of Crude Petroleum

Boiling Range (°C)	Number of Carbons	Fraction	Use
under 30°	2–4	petroleum gas	LP gas for heating
30°–180°	4–9	gasoline	motor fuel
160°–230°	8–16	kerosene	heating, jet fuel
200°–320°	10–18	diesel	motor fuel
300°–450°	16–30	heavy oil	heating, lubrication
>300° (vacuum)	>25	petroleum "jelly,"	
		paraffin "wax"	
residue	>35	asphalt	