KMPHOR-Compiled

Structure and Bonding

What is Organic Chemistry

- The chemistry of compounds containing Carbon
- The scope of Organic Chemistry
  - Molecular Structure: How e^- bonds forms

Periodic Table

- Period - Based on electron energy level
- Groups/Families - Based on number of valence electrons
- Group VIIA - Inert
- Outermost electrons - Valence electrons
- Inner electrons- Core electrons, innately stable
- Valence electrons are used in chemical reactions- they are the electrons that participate in chemical bonding.

Group	# of Valence Electrons
IA	1
IIA	2
IIIB	3
IVB	4
VB	5
VIB	6
VIIB	7
VIIIB	8
IB	1
IIB	2
IIIA	3
IVA	4
VA	5
VIA	6
VIIA	7

Group	# of Valence Electrons
VIIA	8 (Except Helium)

Bonding

Ionic bonds - transfer of electrons from one element to another.

Covalent bonds - sharing of electrons between two nuclei.

Ionic Bonds

An ionic bond generally occurs when elements with extra electrons in its valence share combine with elements that are missing electrons.

They try to obtain an electron configuration closest to the nearest noble gas near them.

Isoelectronic - same electron structure.

NaCl- Na gives away an electron to Cl

$[\mathrm{Na}]^{+}[\mathrm{Cl}]^{-}$

One is on the far left, one is on the far right, except noble gases.

Covalent Bonding

Occurs with elements like Carbon in the middle of the periodic table that have similar electronegativity,

Covalent bonds also occur between two of the same elements from the sides of the table.

A covalent bond is a two electron bond, and those that form it are called molecules.

H_2

Hydrogen atom bonded with another hydrogen atom. This forms one covalent bond.

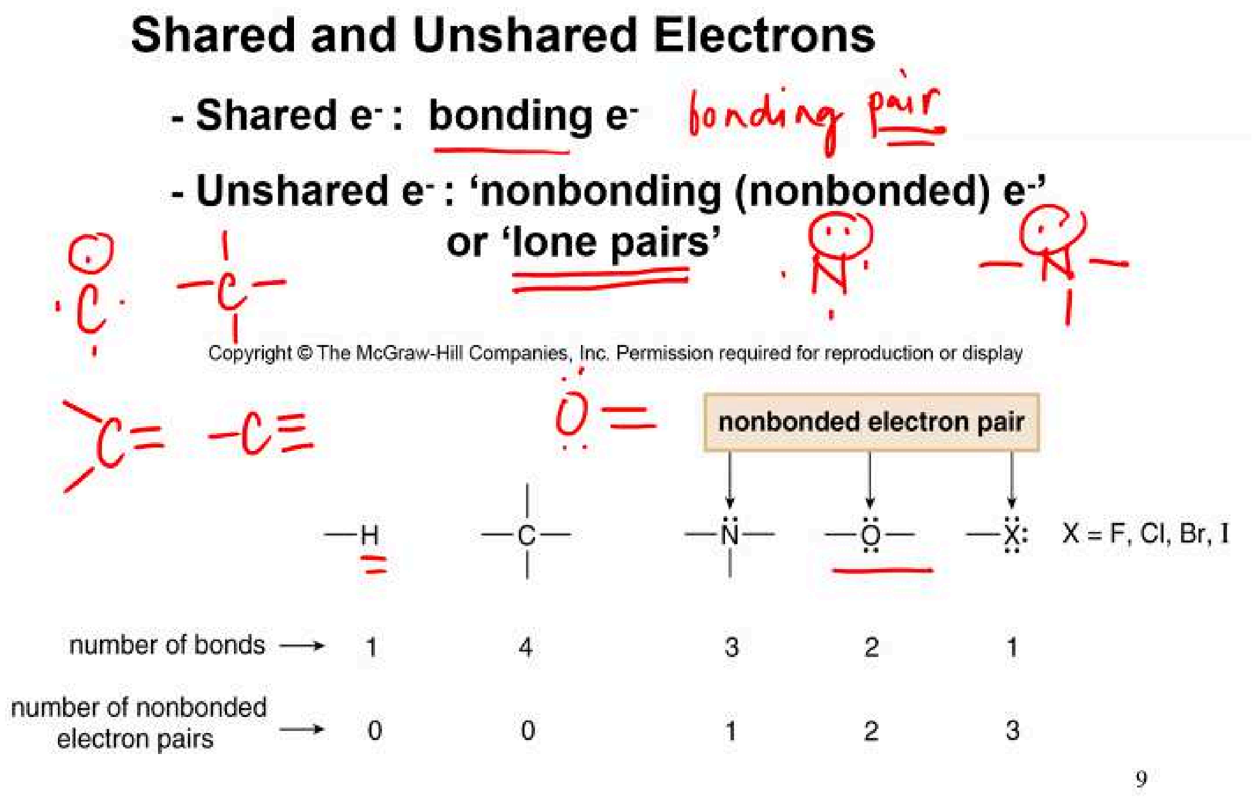
$\mathrm{H}\cdot + \mathrm{H}\cdot\ \mathrm{H}:\mathrm{H}$ or $\mathrm{H}-\mathrm{H}$ - Two electron bond

Both of these hydrogen atoms each have two electrons now in its outer shell, being isoelectronic with Helium.

Shared electrons

- Shared e^{-}: bonding e^{-}

- Unshared e^-: nonbonding e^-, or lone pairs



Shared and Unshared Electrons

- Shared e^- : bonding e^- bonding pair
- Unshared e^- : 'nonbonding (nonbonded) e^-' or 'lone pairs'

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nonbonded electron pair

	—H	—C—	—N—	—O—	—X:
number of bonds →	1	4	3	2	1
number of nonbonded electron pairs →	0	0	1	2	3

X = F, Cl, Br, I

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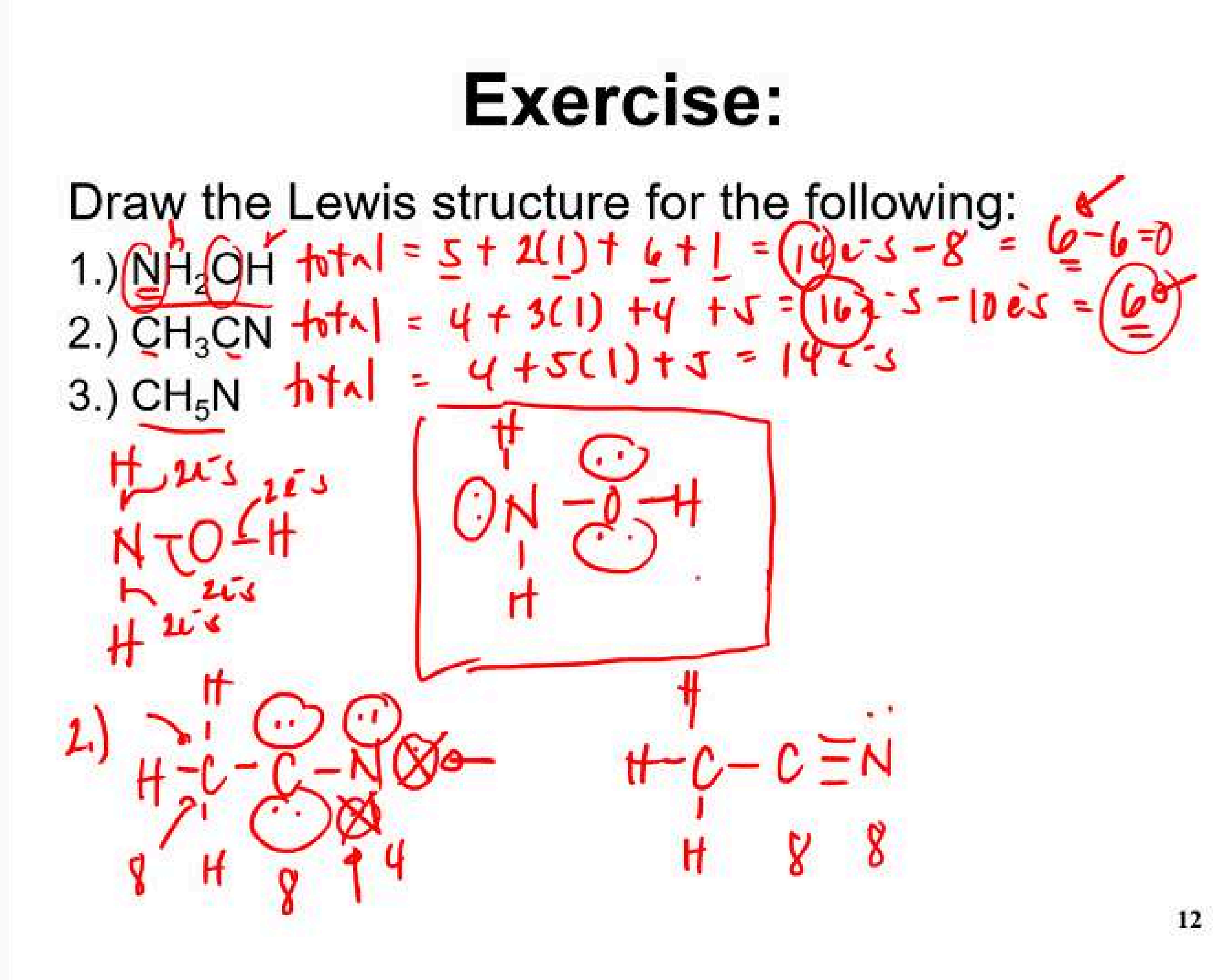
How to Draw a Lewis Structure

1. Arrange atoms next to each other that you think are bonded together
    1. Always place hydrogen and halogens on the periphery because they form only one bond each.
    2. Place no more atoms around an atom than the number of bonds it usually forms.

More tips:

1. Draw skeletal structure of compound showing what atoms are bonded to each other. Put least electronegative element in the center.
2. Count total number of valence e^-. Add 1 for each negative charge. Subtract 1 for each positive charge.
3. Complete an octet for all atoms except hydrogen.
4. If structure contains too many electrons, form double and triple bonds on central atom as needed.

You cannot add lone pairs.



Exercise:

Draw the Lewis structure for the following:

1.) NH_2OH total = 5 + 2(1) + 6 + 1 = 14 e-s − 8 = 6 − 6 = 0

2.) CH_3CN total = 4 + 3(1) + 4 + 5 = 16 e-s − 10 e-s = 6

3.) CH_5N total = 4 + 5(1) + 5 = 14 e-s

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Exceptions to the Octet Rule

- Elements in Group 2A and 3A do not follow the octet rule.
  - Beryllium shares its two electrons - Group 2A
  - Boron shares its three electrons - Group 3A
- Elements in the Third Row
  - Sulfur as well as phosphorus in the third period do not follow the octet rule.

Formal Charge

- The charge assigned to individual atoms in a Lewis structure.
- Formal Charge = Number of Valence Electrons = Number of electrons an atom "owns" = Unshared electrons + 1/2 shared (bonding) electrons.
  - $FC = VE - LE - \frac{1}{2}BE$
- Number of valence electrons = Group #
- Lone pair electrons - count each dot.
- Bonding pair electrons - count each pair.
  - $GN - LE + B$

Isomers

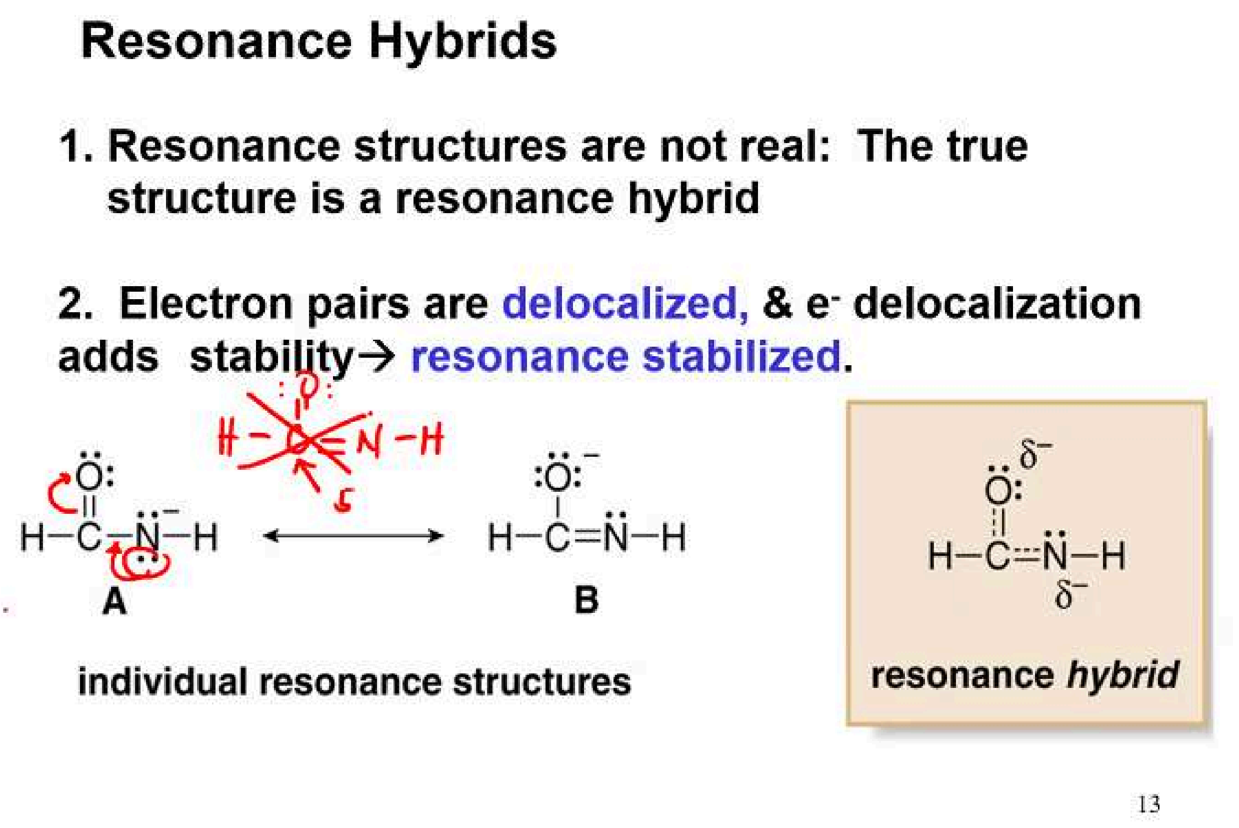
- Isomers: different molecules having the same molecular formula but a different arrangement of atoms
    - Example: Ethanol and Dimethyl Ether - Same molecular formula - C_2H_6O - indicative of isomer.

Resonance Structures

- Resonance structures are not real. An individual resonance structure does not accurately represent the structure of a molecule or ion.
- Resonance structures are not in equilibrium with each other.
- Resonance structures are not isomers. Two isomers differ in the arrangement of both atoms and electrons, whereas resonance structure differ only in the arrangement of electrons.
    - Different permutations of electrons in the structure.
- 2 Lewis structures having the same placement of atoms but a different arrangement of electrons.
- Major and minor contributor: A major contributor is a more stable form (more bonds and fewer charges).
- All single bonds between two atoms are called a σ bond.
    - Any additional bond to a σ bond becomes a π bond.
        - 1 - 1 σ bond
        - 2 - 1 σ bond 1 π bond
        - 3- 1 σ bond 2 π bond
- π electrons are capable of delocalization
- You want to keep as few charges as possible.
- Minor contributors - ones with more charges.

Resonance Hybrids

- Resonance structures are not real: The true structure is a resonance hybrid.
- Electron pairs are delocalized, electron delocalization adds stability -> resonance stabilized.
- Never form 5 bonds with Carbon.



Resonance Hybrids

1. Resonance structures are not real: The true structure is a resonance hybrid

2. Electron pairs are delocalized, & e$^-$ delocalization adds stability→ resonance stabilized.

individual resonance structures

resonance *hybrid*

- True form would be two partial bonds on O and N, and O and N carry partial (δ) negative charges.
  - This form contains both properties of resonance A and B.

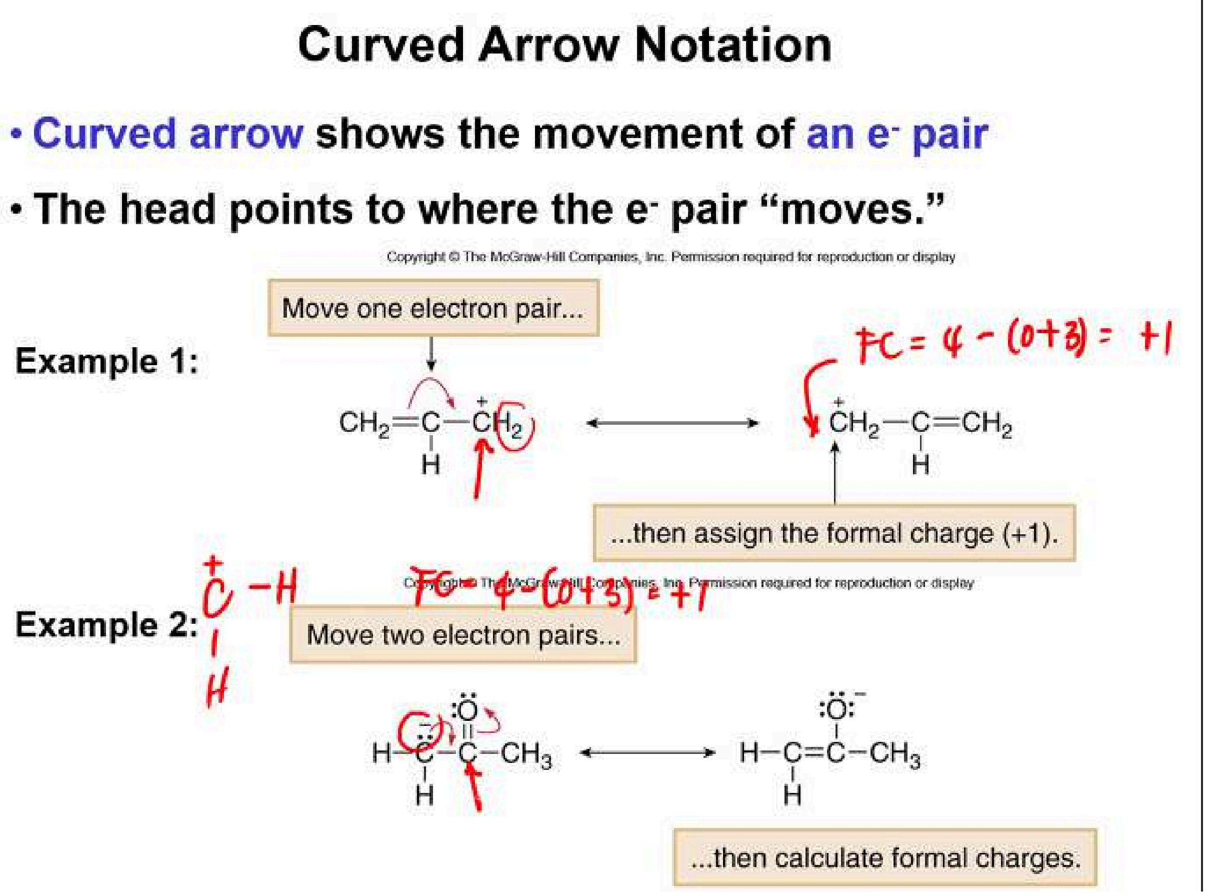
Drawing Resonance Structures

- 2 resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.
- 2 resonance structures must have the same number of unpaired electrons.
- Valid Lewis structure.

Curved Arrow Notation

- Curved arrow shows the movement of an electron pair.

- The head points to where the electron pair moves.



Curved Arrow Notation

- Curved arrow shows the movement of an e^- pair
- The head points to where the e^- pair "moves."

Example 1:

Move one electron pair...

$CH_2{=}C(H){-}\overset{+}{C}H_2 \longleftrightarrow \overset{+}{C}H_2{-}C(H){=}CH_2$

FC = 4 - (0+3) = +1

...then assign the formal charge (+1).

Example 2:

$\overset{+}{C}-H$

|

H

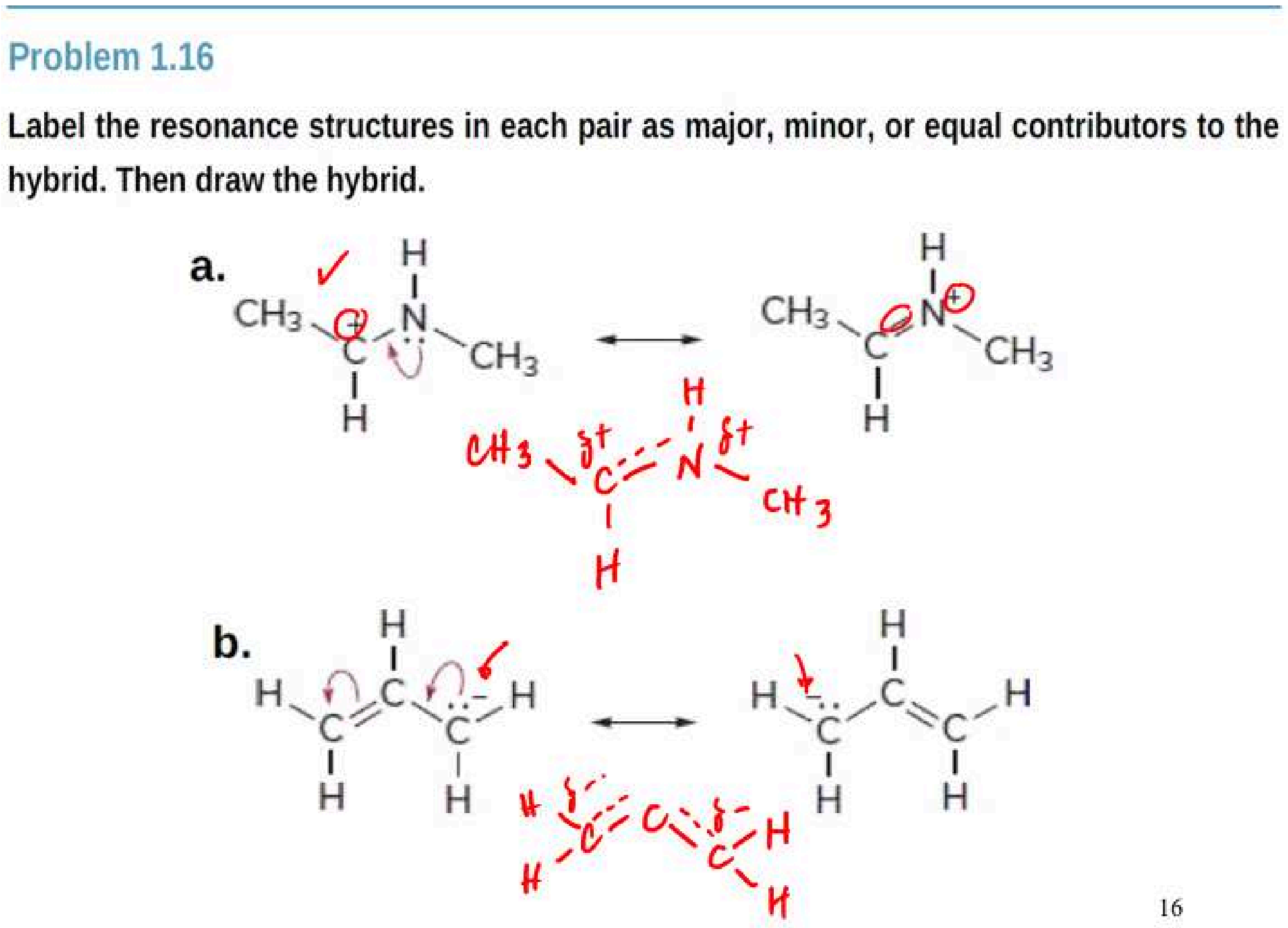
FC = 4-(0+3) = +1

Move two electron pairs...

$H{-}\ddot{C}H^-{-}C({=}O){-}CH_3 \longleftrightarrow H{-}CH{=}C(O^-){-}CH_3$

...then calculate formal charges.

Exercise



Problem 1.16

Label the resonance structures in each pair as major, minor, or equal contributors to the hybrid. Then draw the hybrid.

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+C is more stable because it is more electropositive

Calculating Degrees of Unsaturation

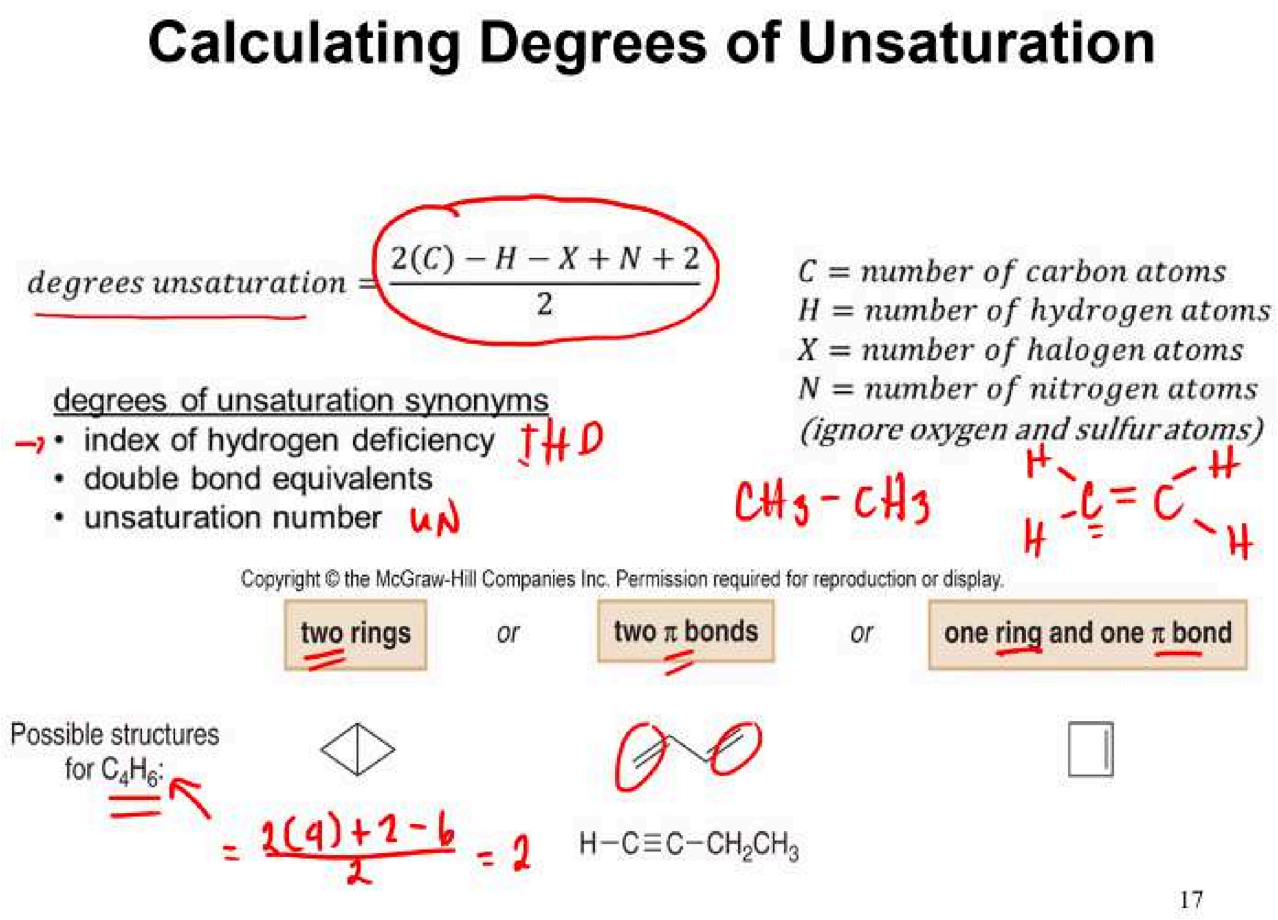
Degrees unsaturation = $\frac{2C-H-X+N+2}{2}$

C = no. of carbon
H = number of hydrogen.
X = number of halogen.
N = number of nitrogen.

Ignore oxygen and sulfur.

Degrees of unsaturation synonyms:

- Index of hydrogen deficiency
- double bond equivalents
- unsaturation number.



Calculating Degrees of Unsaturation

$$\text{degrees unsaturation} = \frac{2(C) - H - X + N + 2}{2}$$

C = number of carbon atoms
H = number of hydrogen atoms
X = number of halogen atoms
N = number of nitrogen atoms
(ignore oxygen and sulfur atoms)

degrees of unsaturation synonyms

- index of hydrogen deficiency IHD
- double bond equivalents
- unsaturation number UN

CH_3-CH_3

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two rings or two π bonds or one ring and one π bond

Possible structures for C_4H_6:

$$= \frac{2(4)+2-6}{2} = 2$$

$H-C\equiv C-CH_2CH_3$

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Degrees of Unsaturation for Molecules Containing Heteroatoms

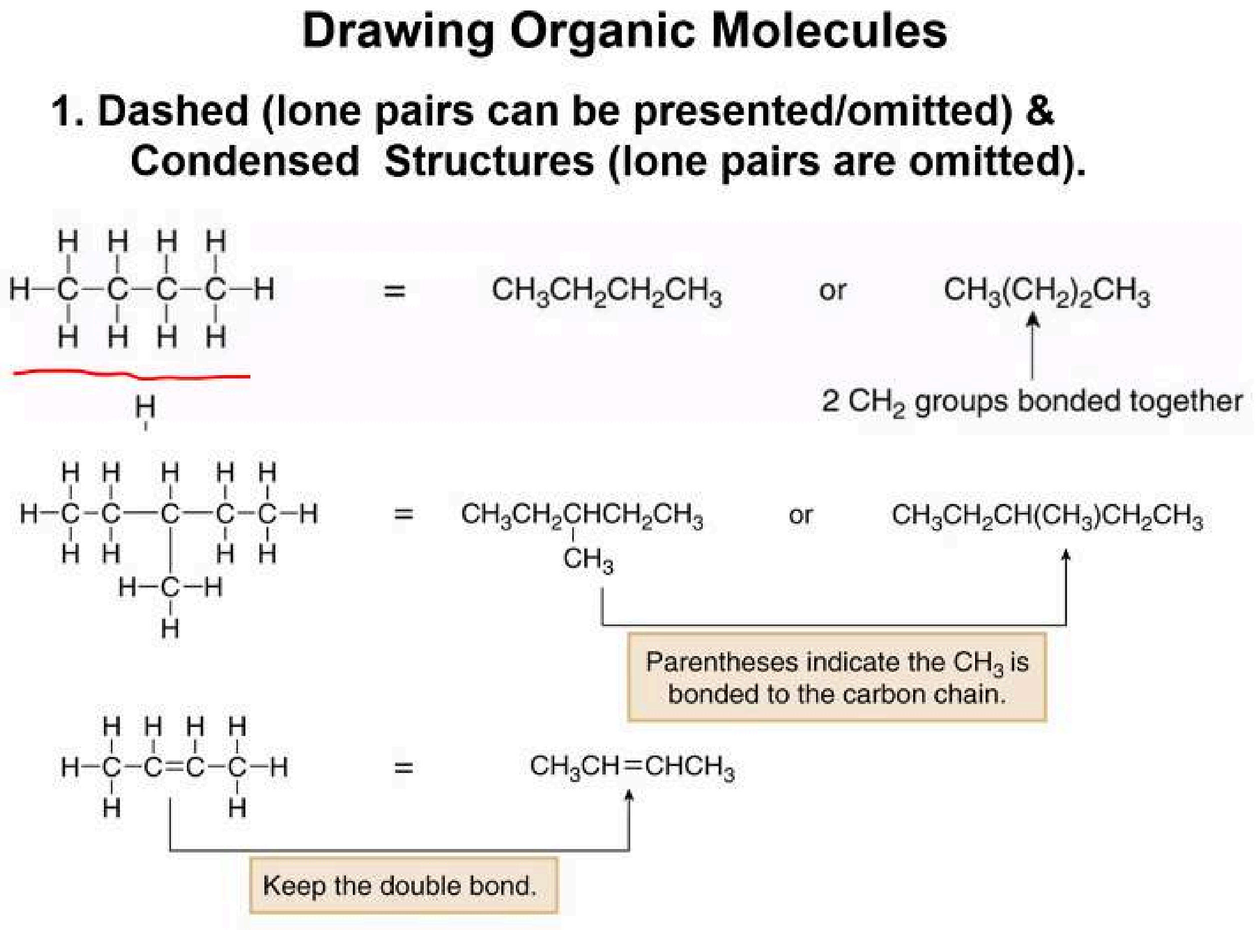
- Ignore O atoms in the molecule

Drawing Organic Molecules

Condensed Structures

- Carbon is tetravalent.
- All of the atoms are drawn in, but the two electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms which they are bonded.
- Parenthesis are used around similar groups bonded to the same atom.

- Lone pairs are omitted.



Drawing Organic Molecules

1. Dashed (lone pairs can be presented/omitted) & Condensed Structures (lone pairs are omitted).

= $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

2 CH_2 groups bonded together

= $CH_3CH_2\underset{|\atop CH_3}{C}HCH_2CH_3$ or $CH_3CH_2CH(CH_3)CH_2CH_3$

Parentheses indicate the CH_3 is bonded to the carbon chain.

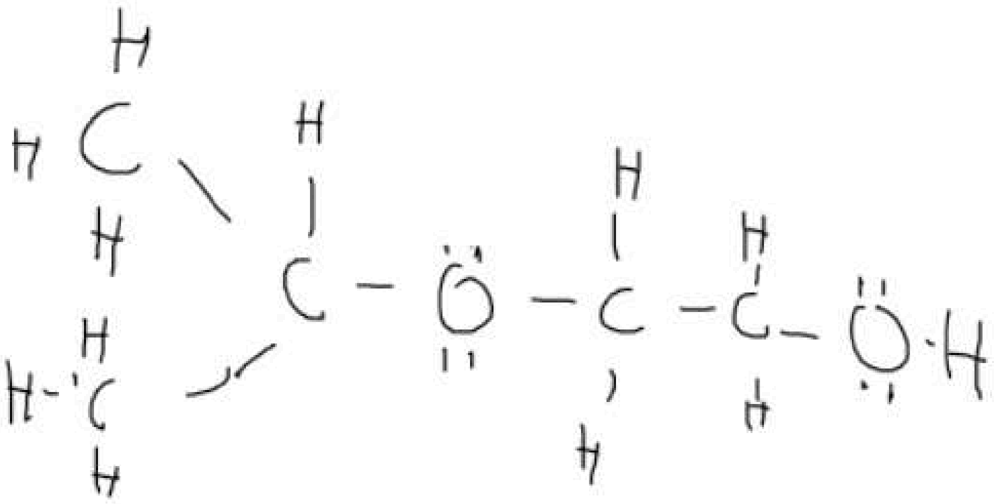
= $CH_3CH{=}CHCH_3$

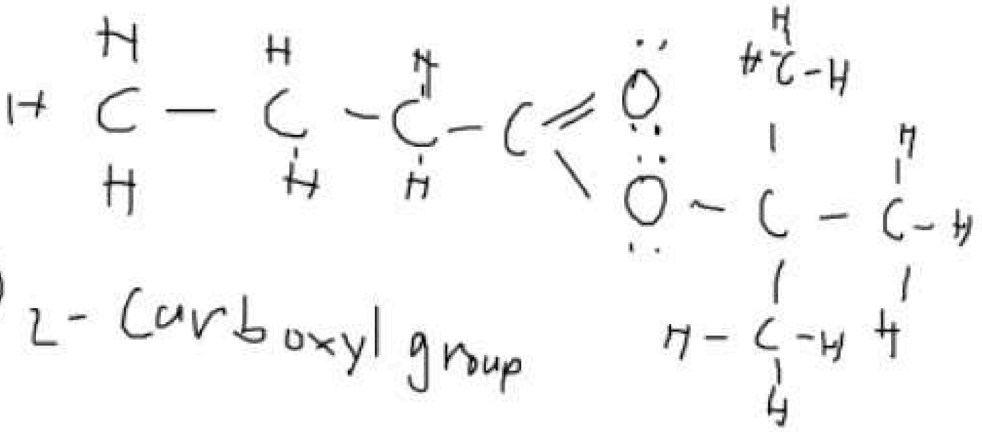
Keep the double bond.

Convert each condensed formula to a Lewis structure.

a. $(CH_3)_2CHOCH_2CH_2CH_2OH$

b. $CH_3(CH_2)_2CO_2C(CH_3)_3$





CO_2- Carboxyl group

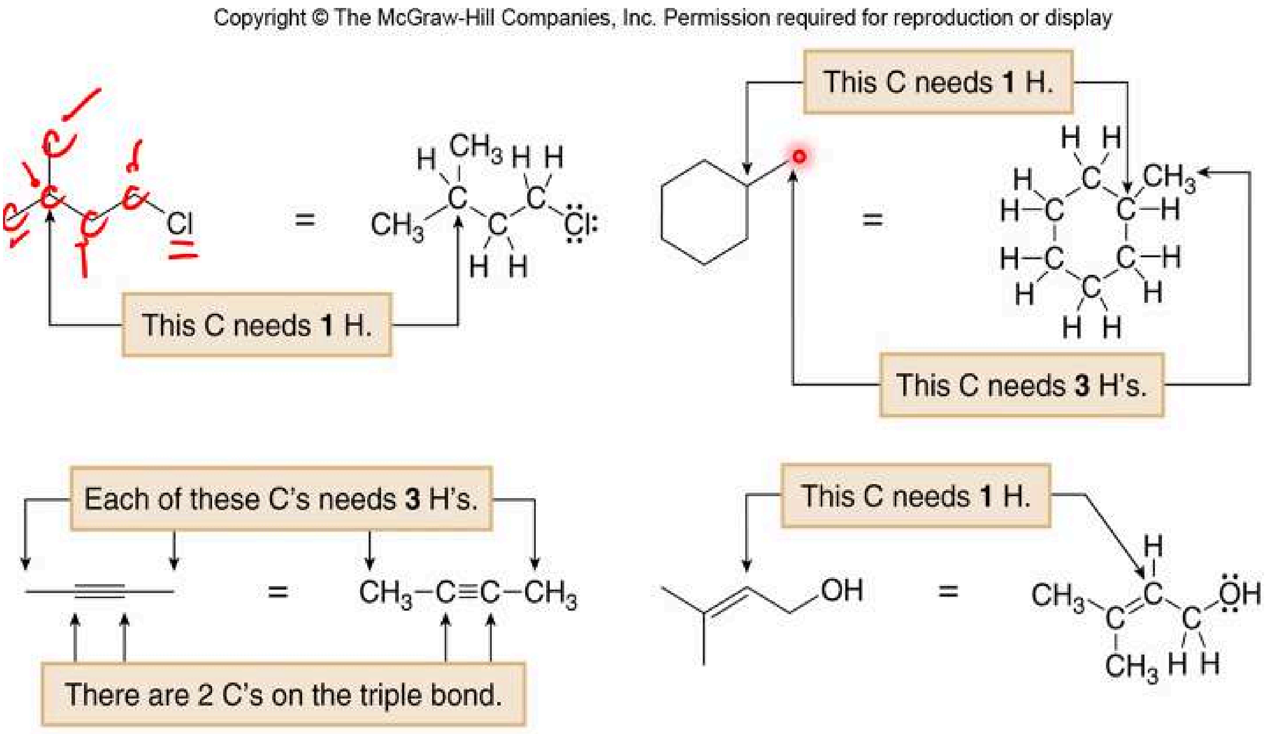
Questions

- Drawing resonance structures
- degrees of unsaturation

Skeletal Structures

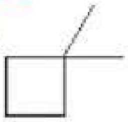
- Assume a carbon atom is located at the junction of any two lines or at the end of any line.
- Assume each carbon has enough hydrogens to make it tetravalent.
- Draw in all heteroatoms and the hydrogens directly bonded to them.
  - Heteroatom - not carbon or hydrogen.

2. Skeletal Structures

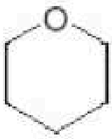


Convert each skeletal structure to a complete structure with all C's, H's, and lone pairs drawn in.

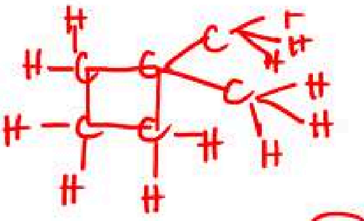
a.

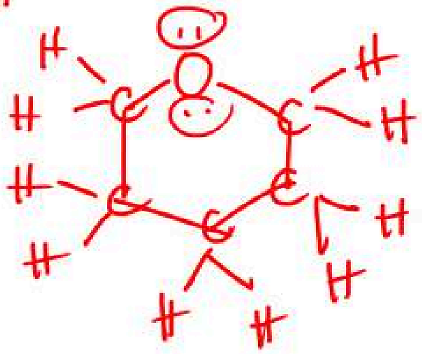


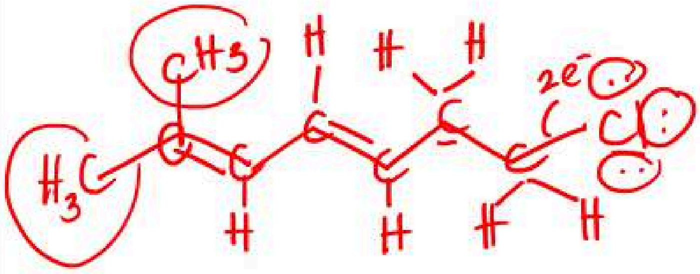
b.



c.







Molecular Geometry

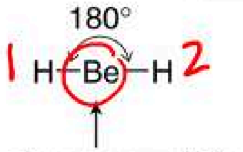
- Valence Shell Electron Pair Repulsion (VSEPR) theory:

- Atoms or lone pair electrons are as far away from each other as possible.

No of Groups	**Geometry**	**Bond Angle**
Two Groups	Linear	180
Three Groups	Trigonal Planar	120
Four Groups	Tetrahedral	109.5

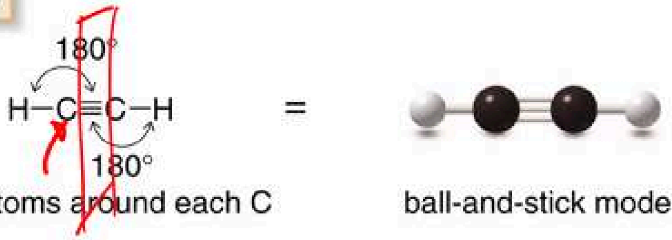
2 Groups Around an Atom

Two linear molecules



two atoms around Be

two groups



two atoms around each C

two groups

ball-and-stick model

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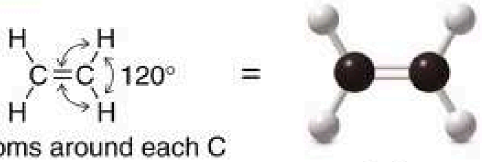
3 Groups Around an Atom

Two trigonal planar molecules

three atoms around B

three groups

All three B−F bonds lie in one plane.



three atoms around each C

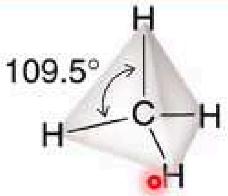
three groups

ethylene

All six atoms lie in one plane.

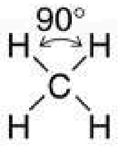
4 Groups Around an Atom

Tetrahedral arrangement



preferred geometry
larger H−C−H bond angle

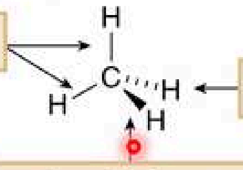
Square planar arrangement



This geometry does ***not*** occur.

Drawing Three-Dimensional Structures

- **Solid line, wedge and dashed line (perspective formula)**

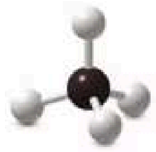


bonds **in** the plane

bond **behind**

bond **in front**

=



ball-and-stick model of CH_4

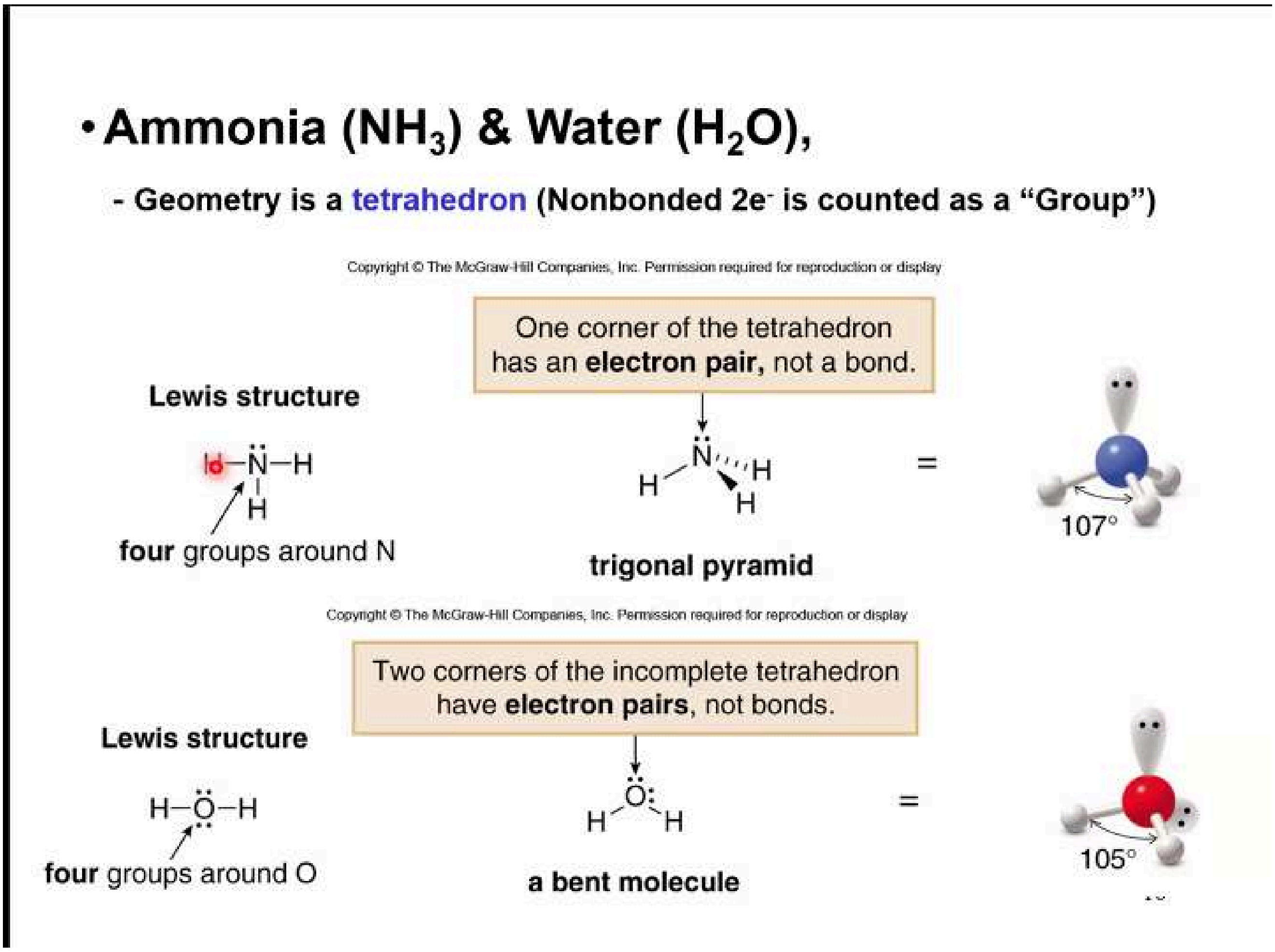
Each drawing has two solid lines, one wedge, and one dashed line.

Solid lines - bonds in the plane

Wedges= bonds in front
Dashed line- bond behind

Ammonia and Water

Geometry is a tetrahedron (Nonbonded 2 electrons are counted as a group)



• **Ammonia (NH_3) & Water (H_2O),**

- Geometry is a tetrahedron (Nonbonded $2e^-$ is counted as a "Group")

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One corner of the tetrahedron has an **electron pair,** not a bond.

Lewis structure

four groups around N

trigonal pyramid

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Two corners of the incomplete tetrahedron have **electron pairs**, not bonds.

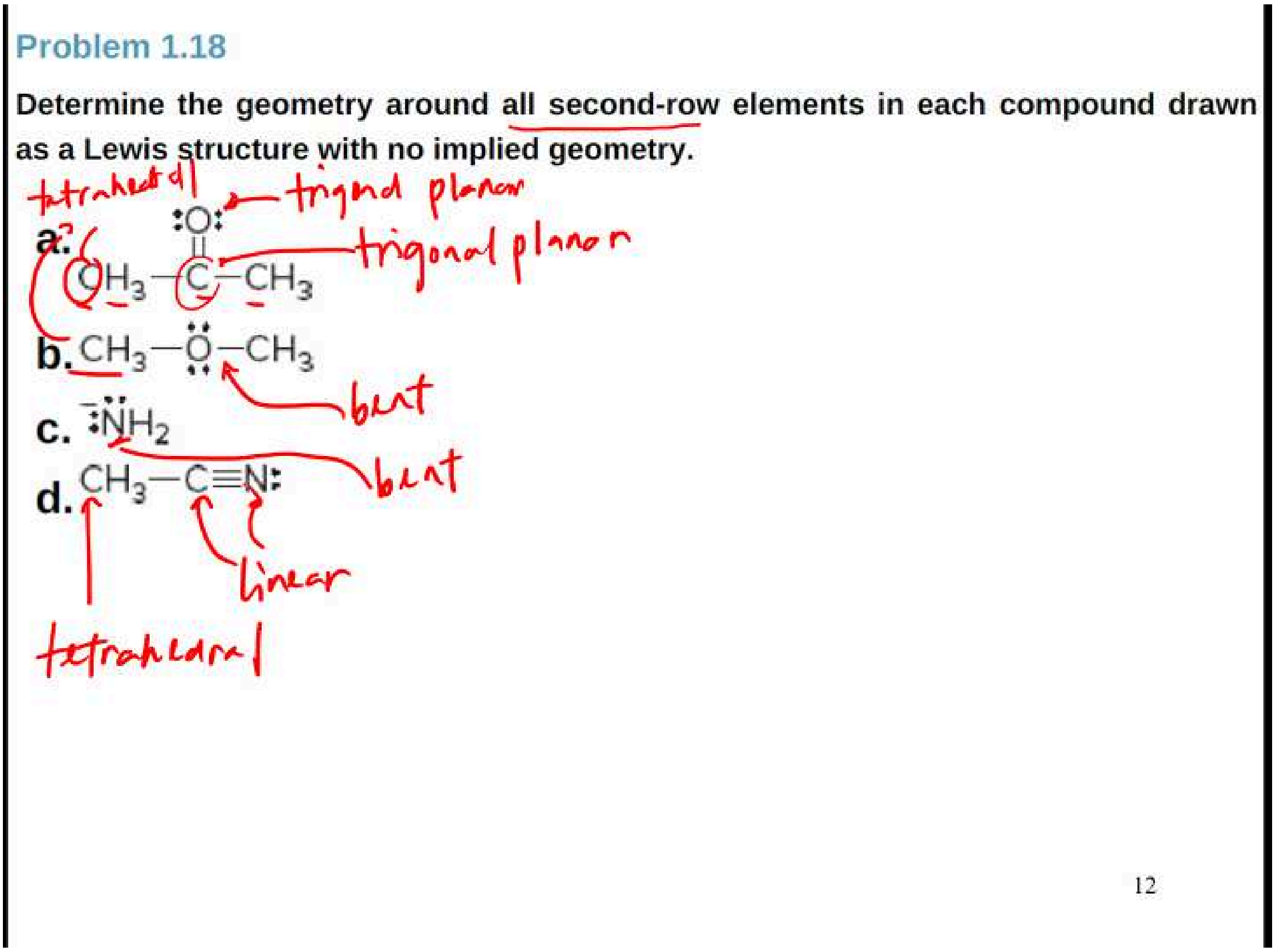
Lewis structure

four groups around O

a bent molecule

Bond angles are different, so NH3 is a trigonal pyramid but not a tetrahedron.

Oxygen is a bent molecule



Problem 1.18

Determine the geometry around all second-row elements in each compound drawn as a Lewis structure with no implied geometry.

a. $CH_3-C(=O)-CH_3$

b. $CH_3-\ddot{O}-CH_3$

c. $:\ddot{N}H_2^-$

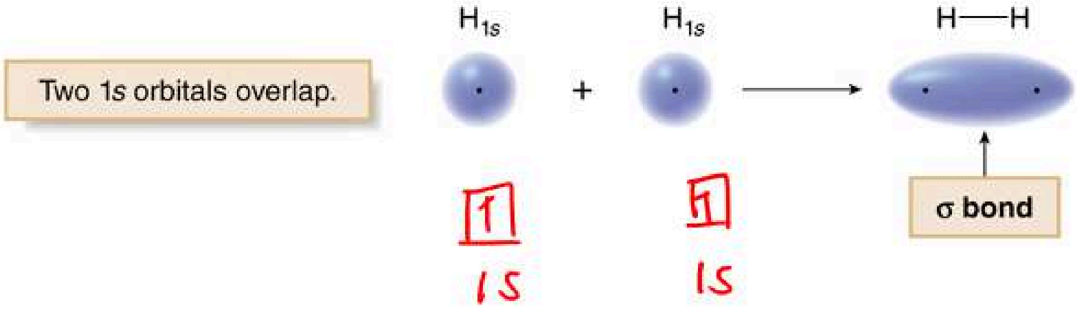
d. $CH_3-C\equiv N:$

Orbital and Bonding

Hydrogen - H_2
one electron, in the s orbital
σ bond - single bond

Orbitals and Bonding

1. Hydrogen (H_2)

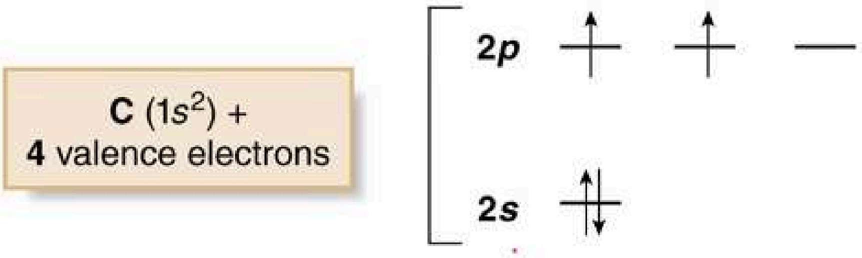


Two 1*s* orbitals overlap.

Carbon:

Orbitals and Bonding: Carbon

1. Electronic configuration of 'Carbon' in its ground state,

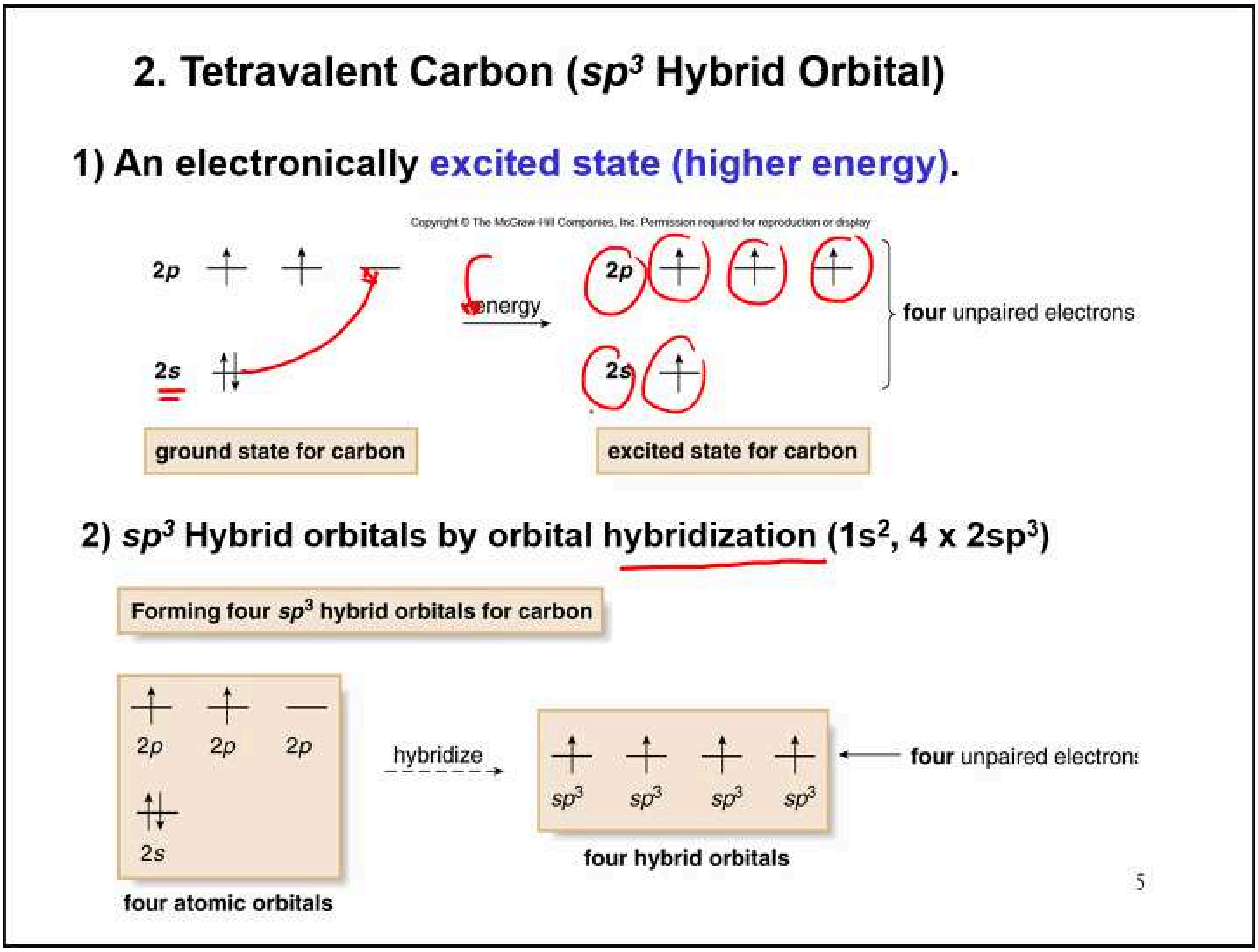


C ($1s^2$) +
4 valence electrons

Atomic orbital ($1s^2$, $2s^2$, $2p^2$)

Tetravalent Carbon

- An electronically excited state (higher energy)
- sp^3 hybrid orbital



2. Tetravalent Carbon (sp^3 Hybrid Orbital)

1) An electronically excited state (higher energy).

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ground state for carbon

excited state for carbon

2) sp^3 Hybrid orbitals by orbital hybridization ($1s^2$, 4 x $2sp^3$)

Forming four sp^3 hybrid orbitals for carbon

four atomic orbitals

four hybrid orbitals

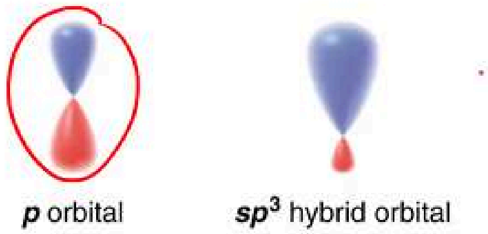
Electron come from s and p, some s characteristic, some p characteristic

sp^3 is somewhere in the middle of s and p in energy state

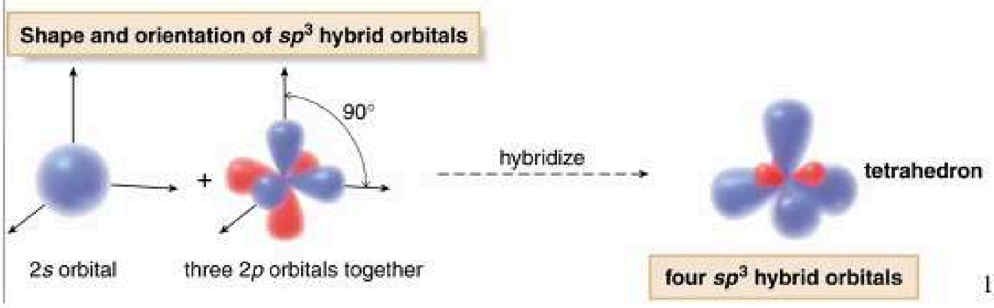
Shape and Orientation Carbon Hybrid Orbitals

1. *sp*^{3} Hybrid Orbitals

1) Shape of *sp*^{3} hybrid orbitals.



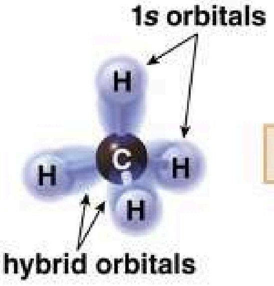
2) 4 *sp*^{3} hybrid orbitals: tetrahedron



CH_4 : *sp*^{3} Hybrid Orbital

- Overlaping of an *sp*^{3} hybrid orbital of C with a 1*s* orbital of H.

ball-and-stick model of CH_4

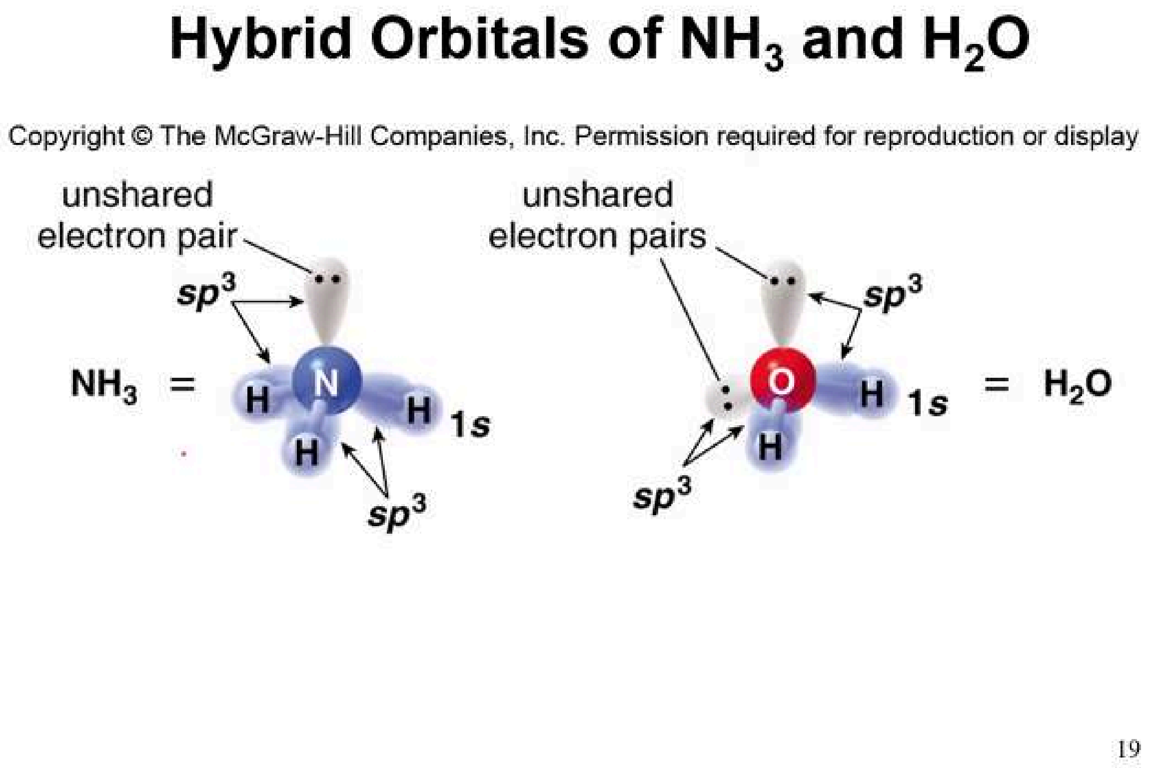


All four C–H bonds are σ bonds.

CH_4 methane

All four C-H bonds are σ bonds

all of them are sp^3 orbital because
hydrogen valence = s orbital
carbon = p orbital



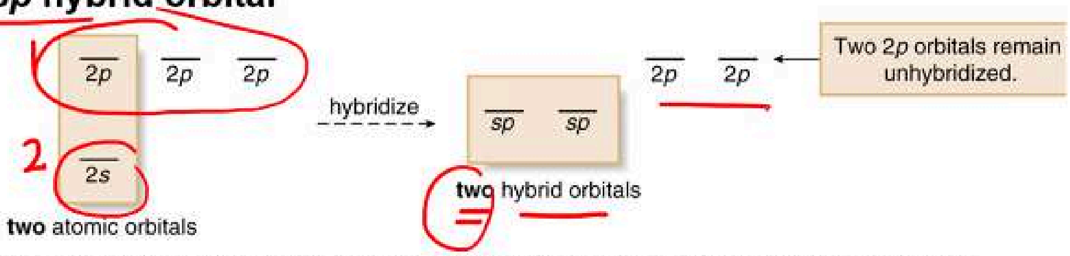
Hybrid Orbitals of NH_3 and H_2O

Both are sp^3 hybrids as well

sp^3 hybrids = 4 groups around atom

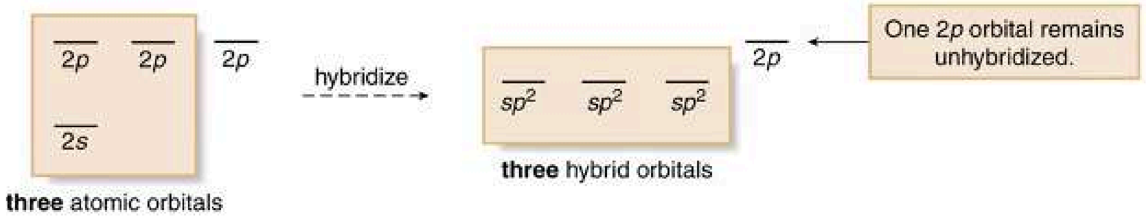
2. sp^2 & sp Hybrid Orbitals

1) *sp* hybrid orbital



- Forming **two *sp* hybrid orbitals** uses **one 2*s*** and **one 2*p* orbital,** leaving **two 2*p* orbitals *unhybridized.***

2) sp^2 hybrid orbital



- Forming **three sp^2 hybrid orbitals** uses **one 2*s*** and **two 2*p* orbitals,** leaving **one 2*p* orbital *unhybridized.***

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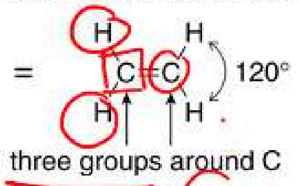
sp^2 Hybrid Orbitals

$CH_2{=}CH_2$ =

ethylene

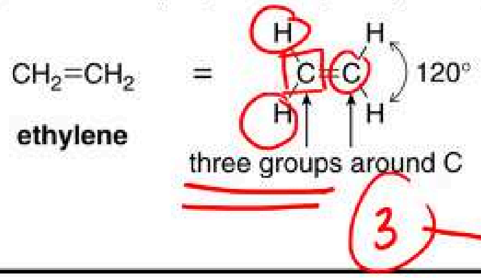


3

Each carbon is trigonal planar.

Each carbon is sp^2 hybridized.

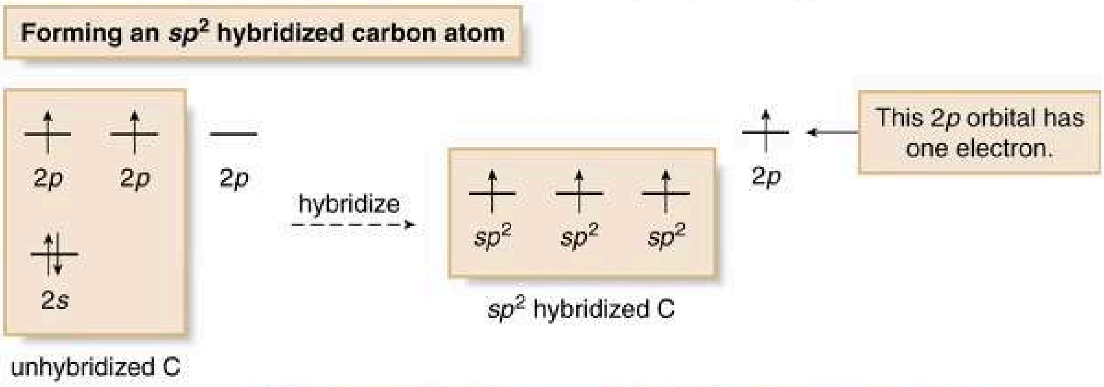
sp^2 Hybrid Orbitals



Each carbon is trigonal planar.

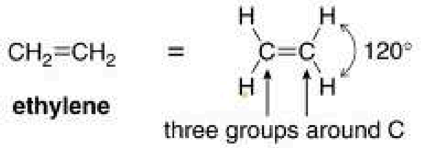
Each carbon is sp^2 hybridized.

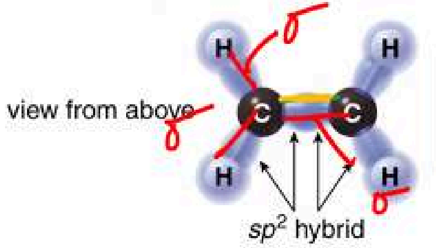
trigonal planar



Walang to sa exam?? I will still study

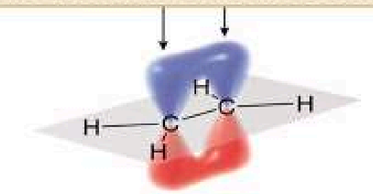
Ethylene: sp^2 Hybrid Orbital



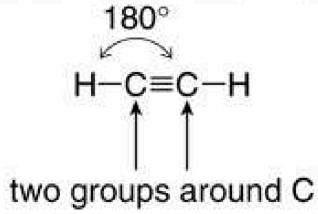


- Each C has three sp^2 hybrid orbitals.
- The C–H bonds and the C–C bond are σ bonds.

Overlap of the 2*p* orbitals forms the second C–C bond.

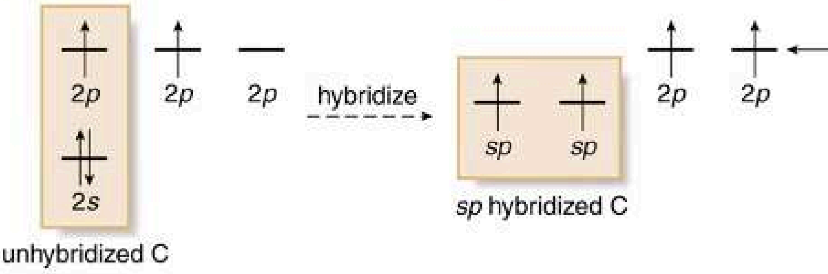


sp Hybrid Orbitals



acetylene

Forming an *sp* hybridized carbon atom

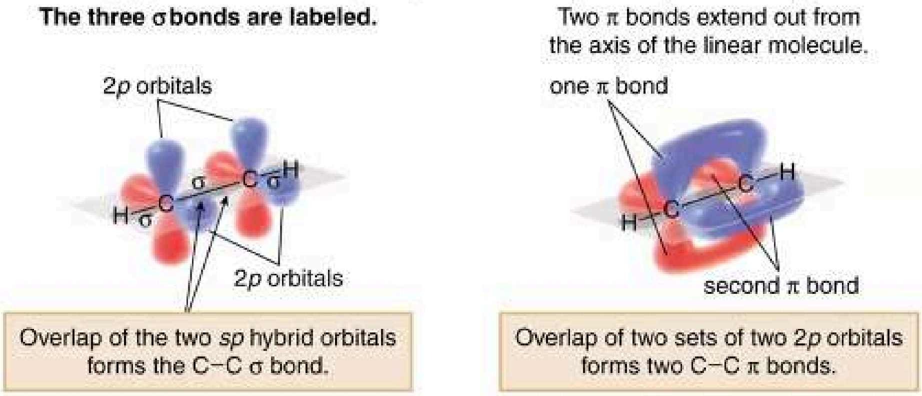


Two 2*p* orbitals have one electron each.

Two groups , so only two sp hybridized carbon atom

sp3 = four groups
sp2 = three groups
sp = two groups

Summary of Bonding in Acetylene



Overlap of the two *sp* hybrid orbitals forms the C–C σ bond.

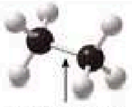
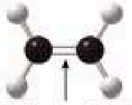
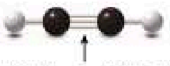
Overlap of two sets of two 2*p* orbitals forms two C–C π bonds.

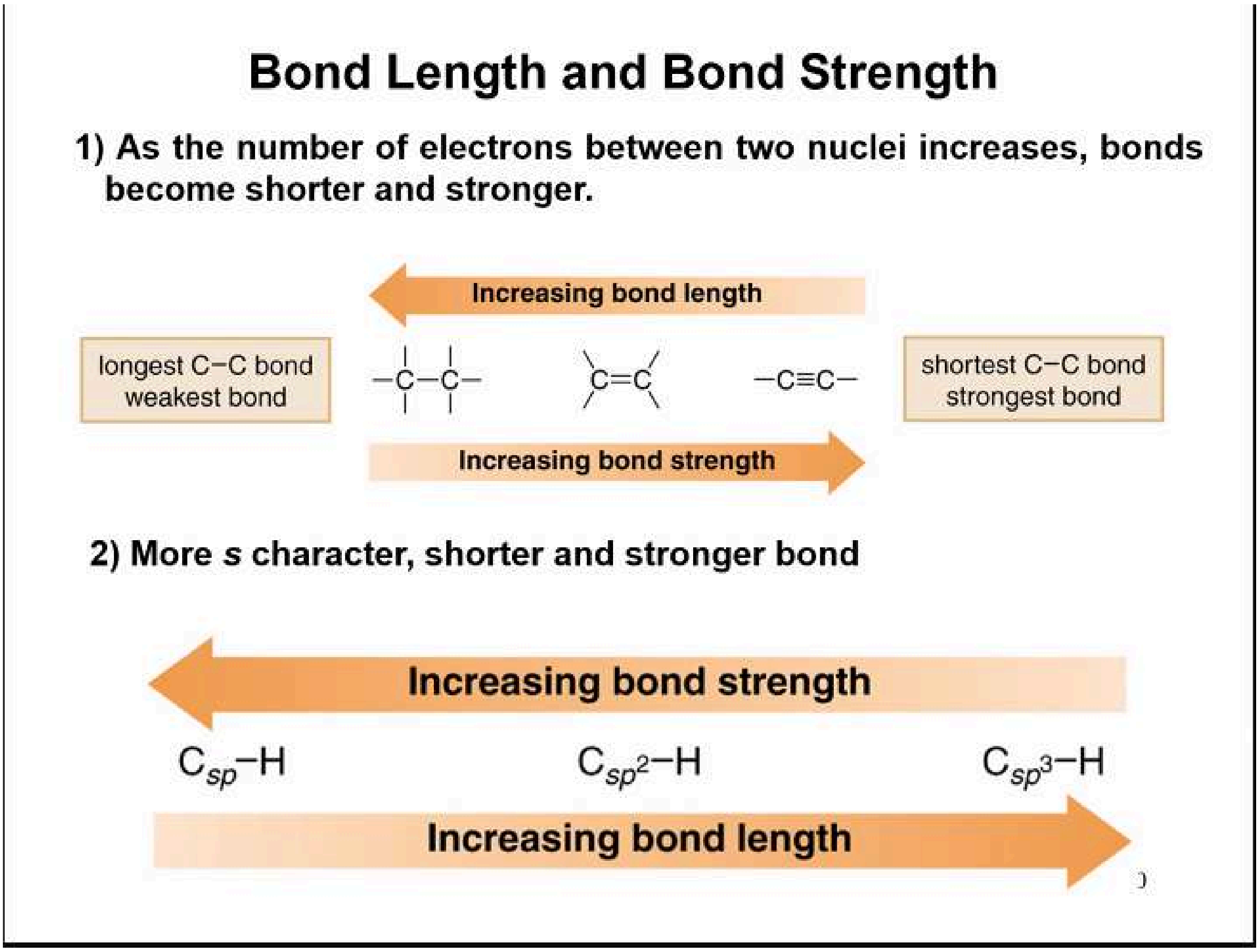
π_{p-p}

$H - C \equiv C - H$

σ_{s-sp} π_{p-p} σ_{sp-sp} σ_{s-sp}

Summary of Covalent Bonding

Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	*sp*^{3}	109.5°	CH_3CH_3 ethane	 one σ bond $C_{sp^3}-C_{sp^3}$
3	*sp*^{2}	120°	$CH_2{=}CH_2$ ethylene	 one σ bond + one π bond $C_{sp^2}-C_{sp^2}$ | $C_{2p}-C_{2p}$
2	*sp*	180°	$HC{\equiv}CH$ acetylene	 one σ bond + two π bonds $C_{sp}-C_{sp}$ | $C_{2p}-C_{2p}$ $C_{2p}-C_{2p}$



Bond Length and Bond Strength

1) As the number of electrons between two nuclei increases, bonds become shorter and stronger.

Increasing bond length

longest C−C bond
weakest bond

shortest C−C bond
strongest bond

Increasing bond strength

2) More *s* character, shorter and stronger bond

Increasing bond strength

C_{sp}−H

C_{sp^2}−H

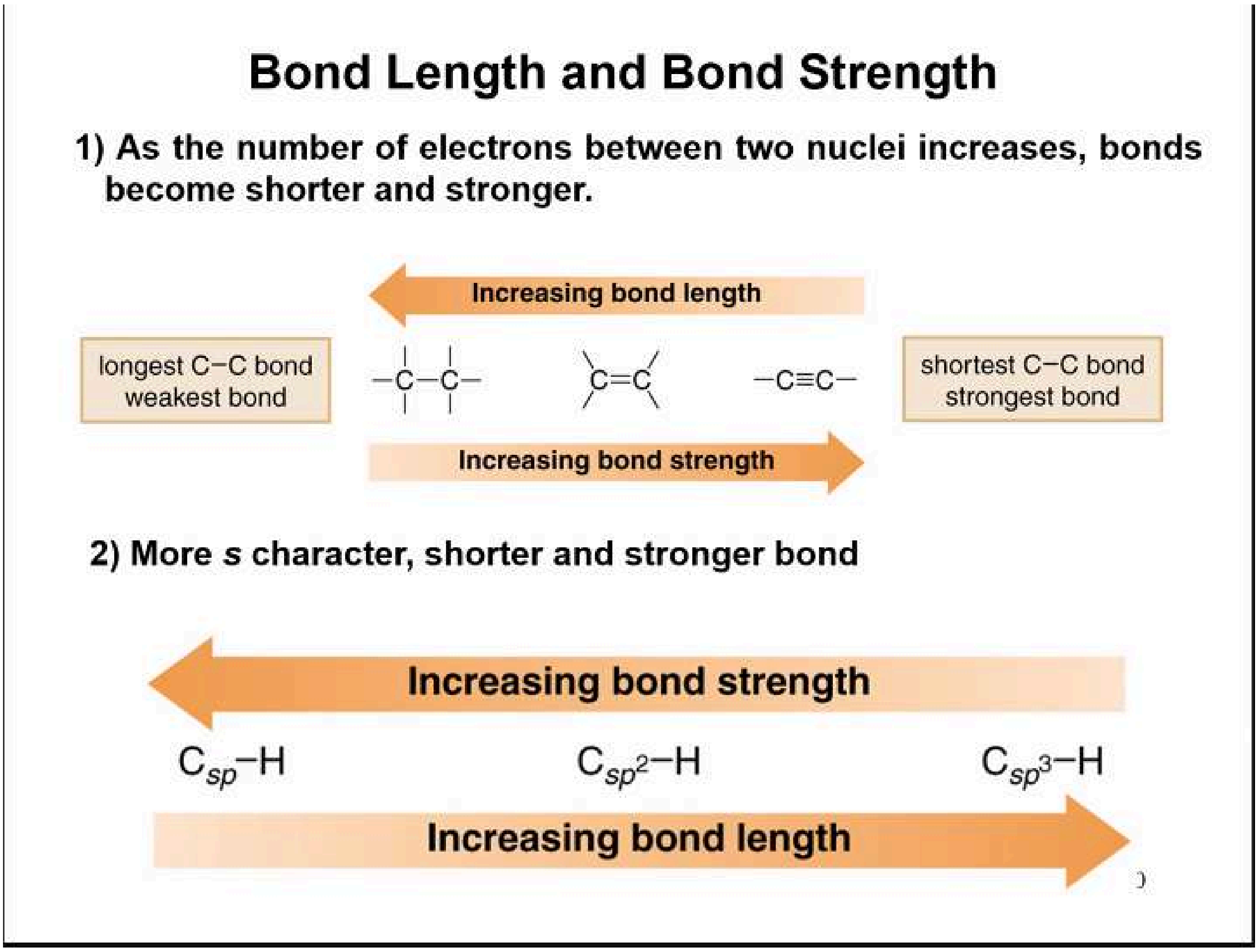
C_{sp^3}−H

Increasing bond length

Bond Length and Bond Structure

1. As the number of electrons between two nuclei increases, bonds become shorter and stronge.

2. More s character, shorter and stronger bond.



Bond Length and Bond Strength

1) As the number of electrons between two nuclei increases, bonds become shorter and stronger.

Increasing bond length

longest C–C bond
weakest bond

$-C\equiv C-$

shortest C–C bond
strongest bond

Increasing bond strength

2) More *s* character, shorter and stronger bond

Increasing bond strength

$C_{sp}-H$ $C_{sp^2}-H$ $C_{sp^3}-H$

Increasing bond length

Percent s-Character

sp	**1 2s**	**2 hybrid**	**50%**
sp2	1 2s	3 hybrid	33%
sp3	1 2s	4 hybrid	25%

Increased percent s character -- Increased bond strength -- Decreased bond length

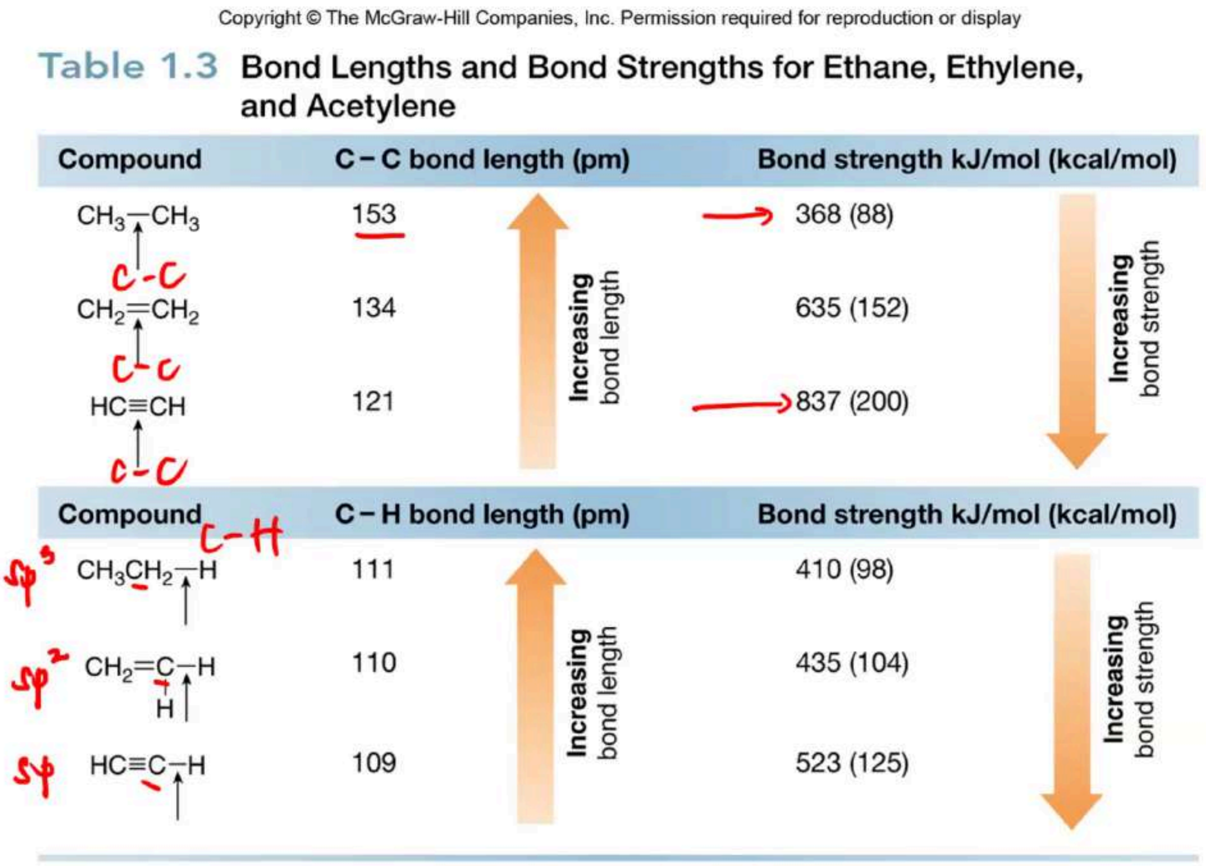


Table 1.3 Bond Lengths and Bond Strengths for Ethane, Ethylene, and Acetylene

Compound	C–C bond length (pm)	Bond strength kJ/mol (kcal/mol)
CH_3-CH_3 C-C	153	368 (88)
$CH_2=CH_2$ C-C	134	635 (152)
$HC\equiv CH$ C-C	121	837 (200)

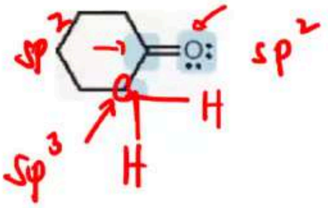
Compound C-H	C–H bond length (pm)	Bond strength kJ/mol (kcal/mol)
sp³ CH_3CH_2-H	111	410 (98)
sp² $CH_2=\underset{H}{C}-H$	110	435 (104)
sp $HC\equiv C-H$	109	523 (125)

Answer each question for cyclohexanone.

a. Determine the hybridization of the highlighted atoms.

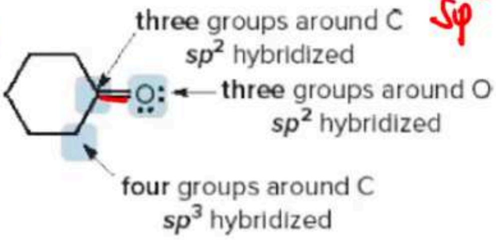
b. What orbitals are used to form the C–O double bond?

c. In what type of orbital does each lone pair reside?



Solution

a.



b.
- **The σ bond is formed from the end-on overlap of C_{sp^2}–O_{sp^2}.**
- **The π bond is formed from the side-by-side overlap of C_{2p}–O_{2p}.**

c. The O atom has three sp^2 hybrid orbitals.

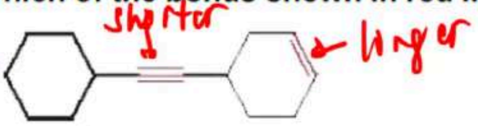
- **One is used for the σ bond of the double bond.**
- **The remaining two sp^2 hybrids are occupied by the lone pairs.**

5

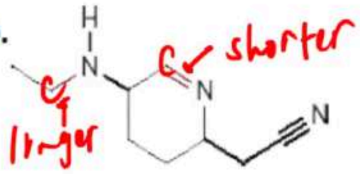
Problem 1.33

Which of the bonds shown in red in each compound or pair of compounds is shorter?

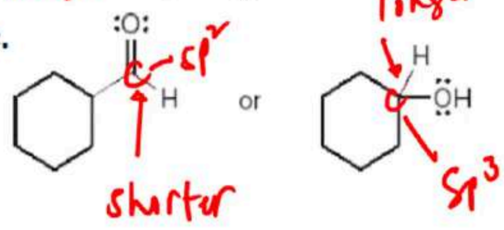
a.



b.



c.



Electronegativity

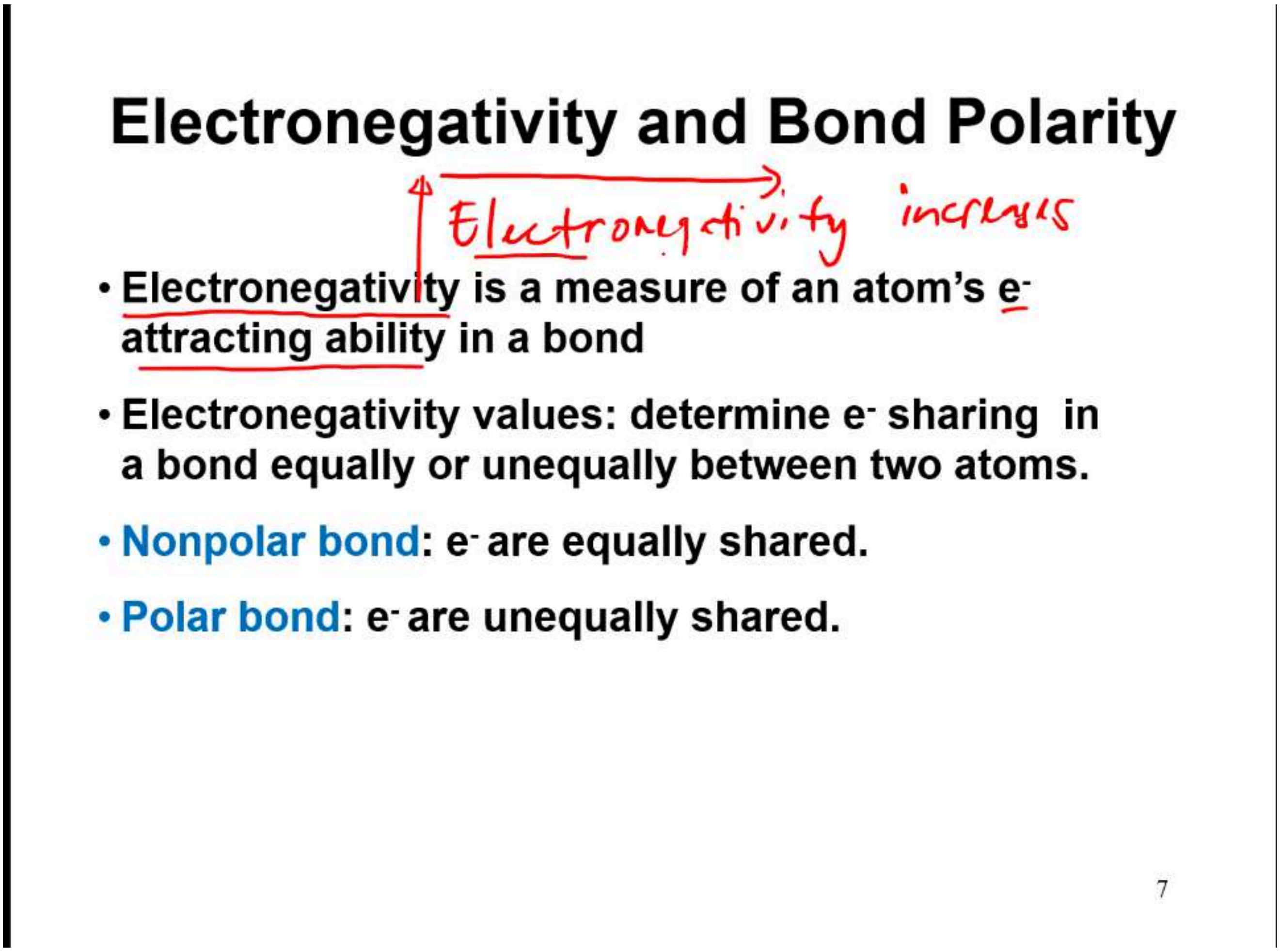
- Electronegativity is a measure of an atoms electron attracting ability in a bond.
- Electronegativity values: determine electron sharing in a bond equally or unequally between two atoms

Non polar bond: electrons are equally shared.

Polar bond: e are unequally shared.

Electronegativity increases from left to right and bottom to top

more pronounced left to right



Electronegativity and Bond Polarity

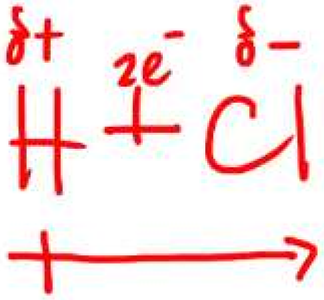
Electronegativity increases

- Electronegativity is a measure of an atom's e^- attracting ability in a bond
- Electronegativity values: determine e^- sharing in a bond equally or unequally between two atoms.
- **Nonpolar bond**: e^- are equally shared.
- **Polar bond**: e^- are unequally shared.

fluorine - 7A - highest electronegativity

noble gases not included

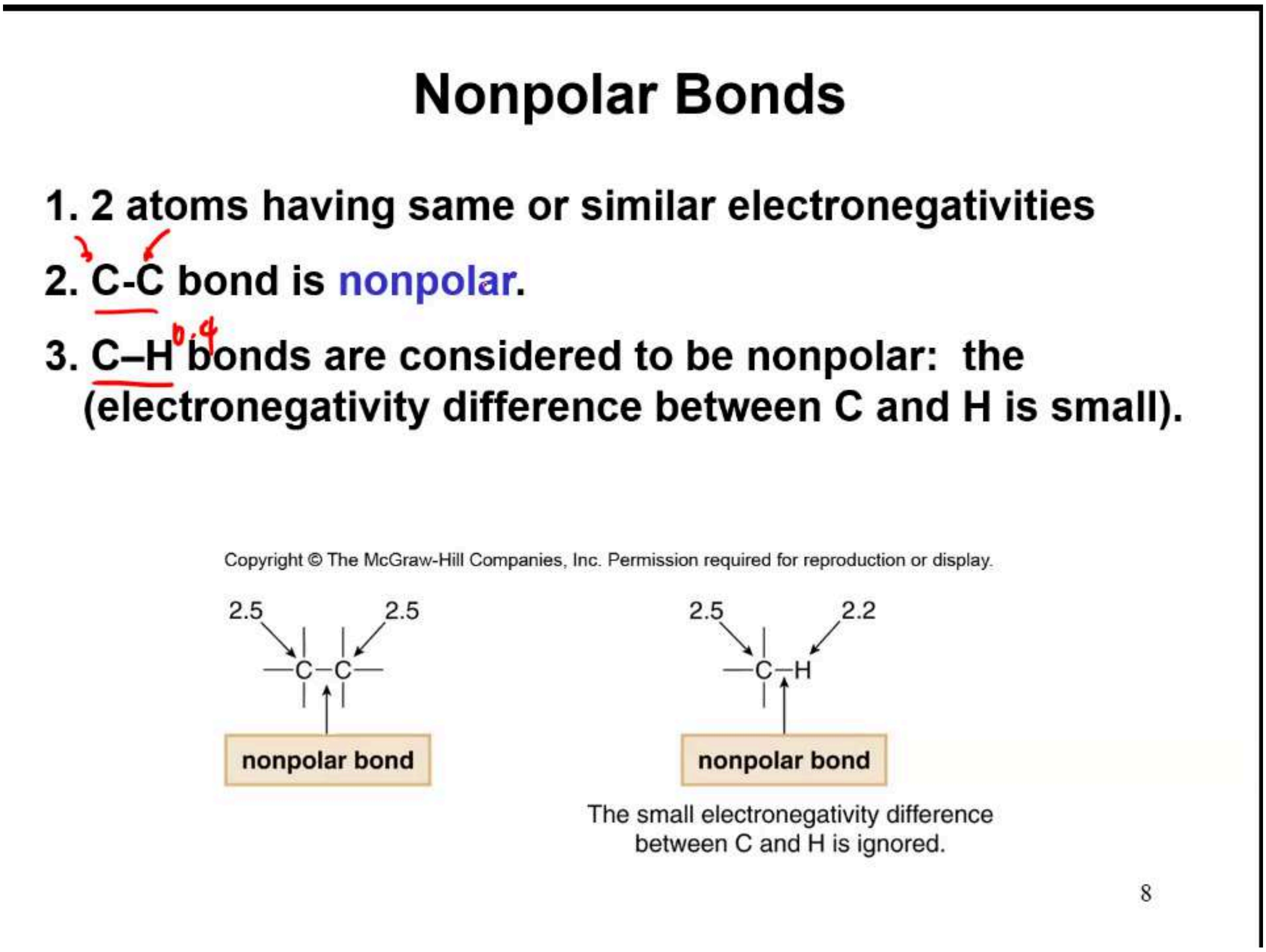
Polar



Non polar

Nonpolar bonds

1. 2 atoms having same or similar electronegativities
2. C-C is nonpolar
3. C-H bonds are considered to be nonpolar: the electronegativity difference between C and H is small.



Nonpolar Bonds

1. 2 atoms having same or similar electronegativities
2. C-C bond is nonpolar.
3. C–H bonds are considered to be nonpolar: the (electronegativity difference between C and H is small).

0.4

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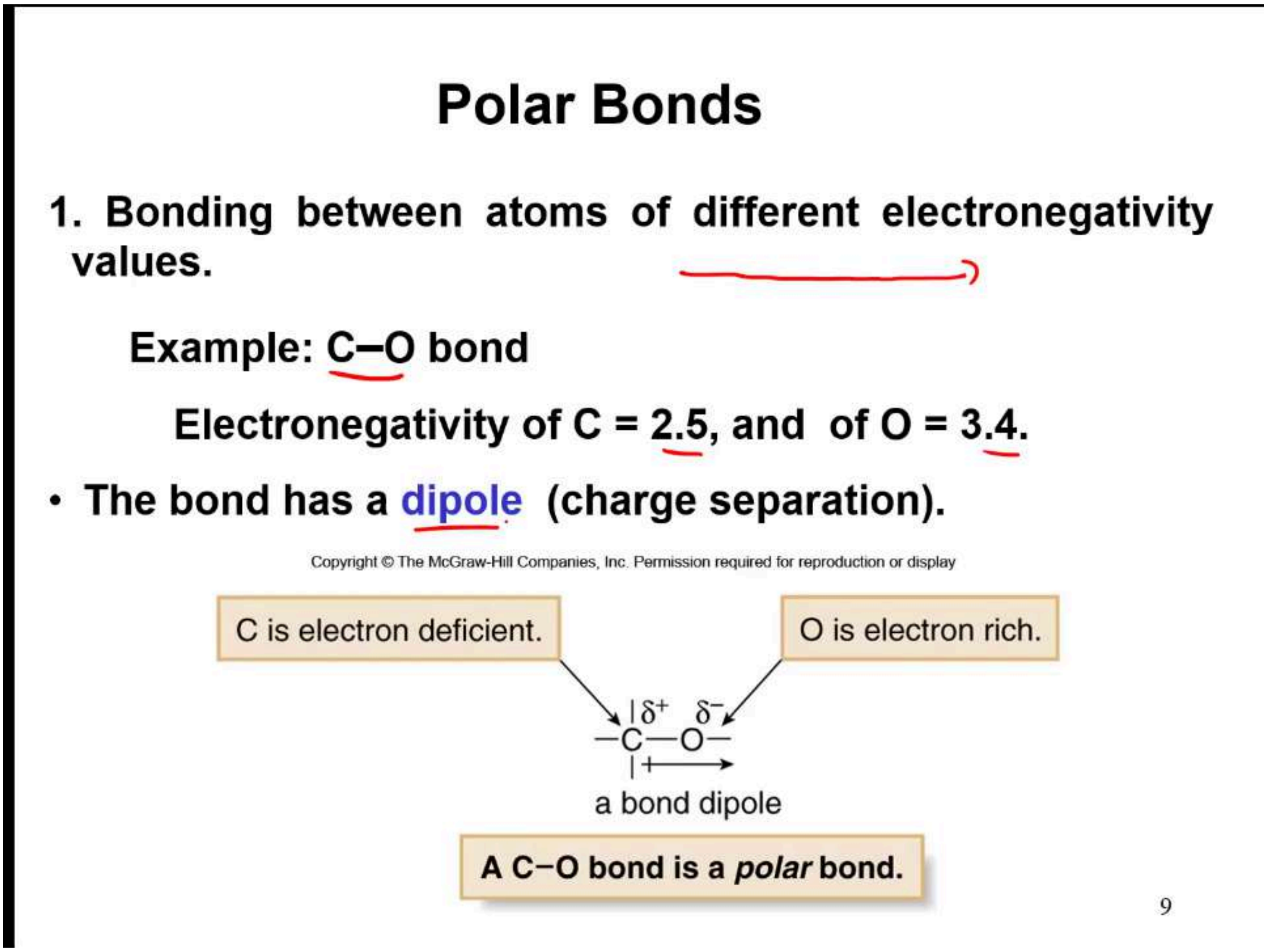
The small electronegativity difference between C and H is ignored.

Polar Bonds

1. Bonding between atoms of different electronegativity values.
    1. Example: C-O bond
        1. Electonegativity of C = 2.5, O = 3.4

The bond has a dipole (charge separation)

Here carbon is electron deficient and oxygen is electron rich



Polar Bonds

1. Bonding between atoms of different electronegativity values.

Example: C–O bond

Electronegativity of C = 2.5, and of O = 3.4.

- The bond has a dipole (charge separation).

C is electron deficient.

O is electron rich.

$$-\overset{|\,\delta^{+}}{\underset{|}{C}}-\overset{\delta^{-}}{O}-$$

$$\longmapsto$$

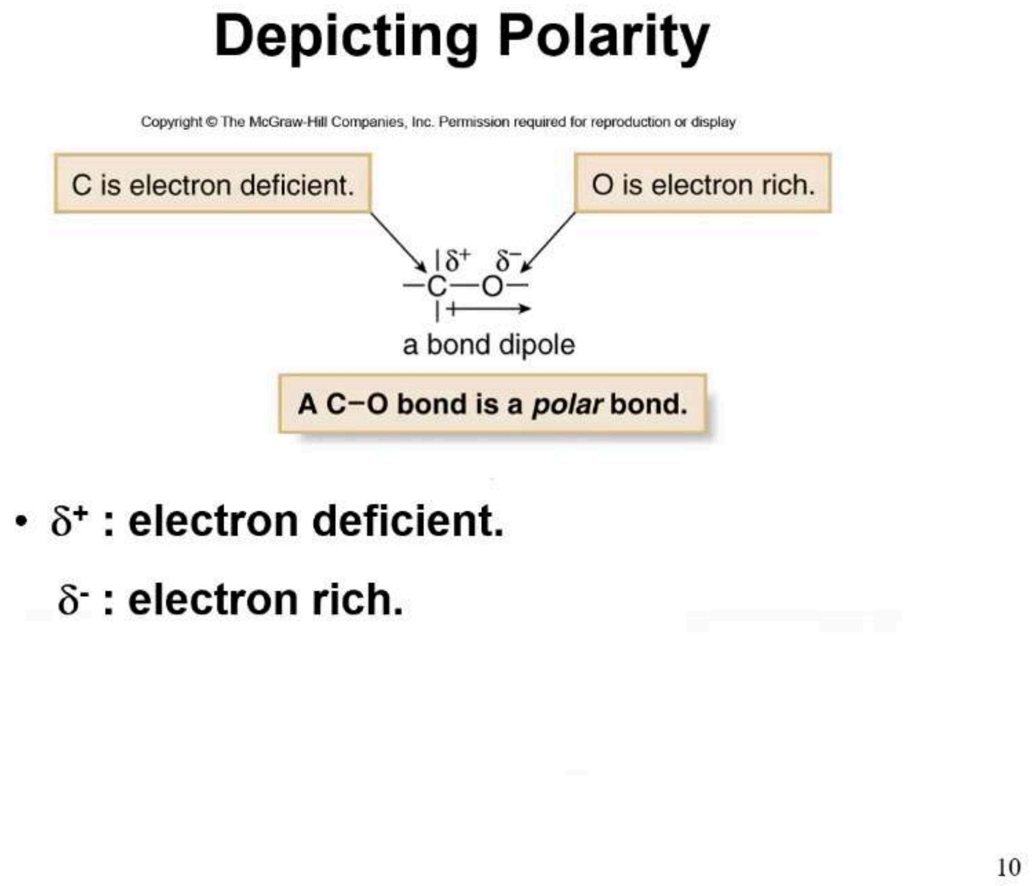
a bond dipole

A C–O bond is a *polar* bond.

Depicting Polarity

δ^+ deficient

δ^- rich



Depicting Polarity

C is electron deficient.

O is electron rich.

a bond dipole

A C–O bond is a *polar* bond.

- **δ+ : electron deficient.**

  δ- : electron rich.

Polarity of Molecules

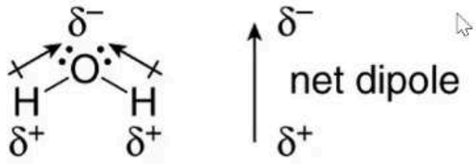
Molecule that has polar bonds does not mean that a molecule is polar

- Vector of the dipole direction: decide if individual dipoles cancel or reinforce each other in space.

Polarity of Molecules

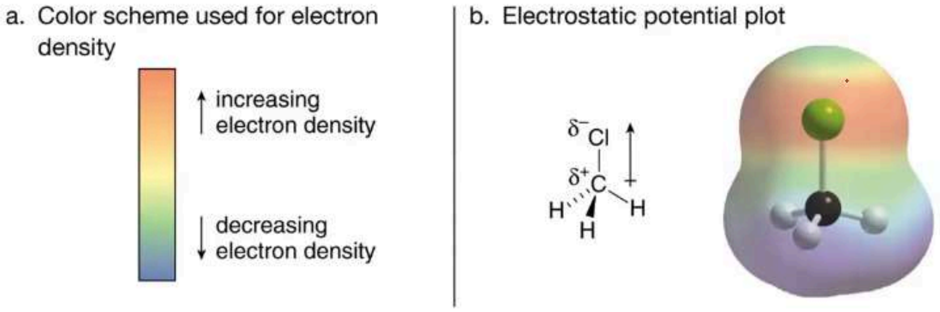
Determination of a net dipole of a molecule

- **Vector of the dipole (direction): decide if individual dipoles cancel or reinforce each other in space.**

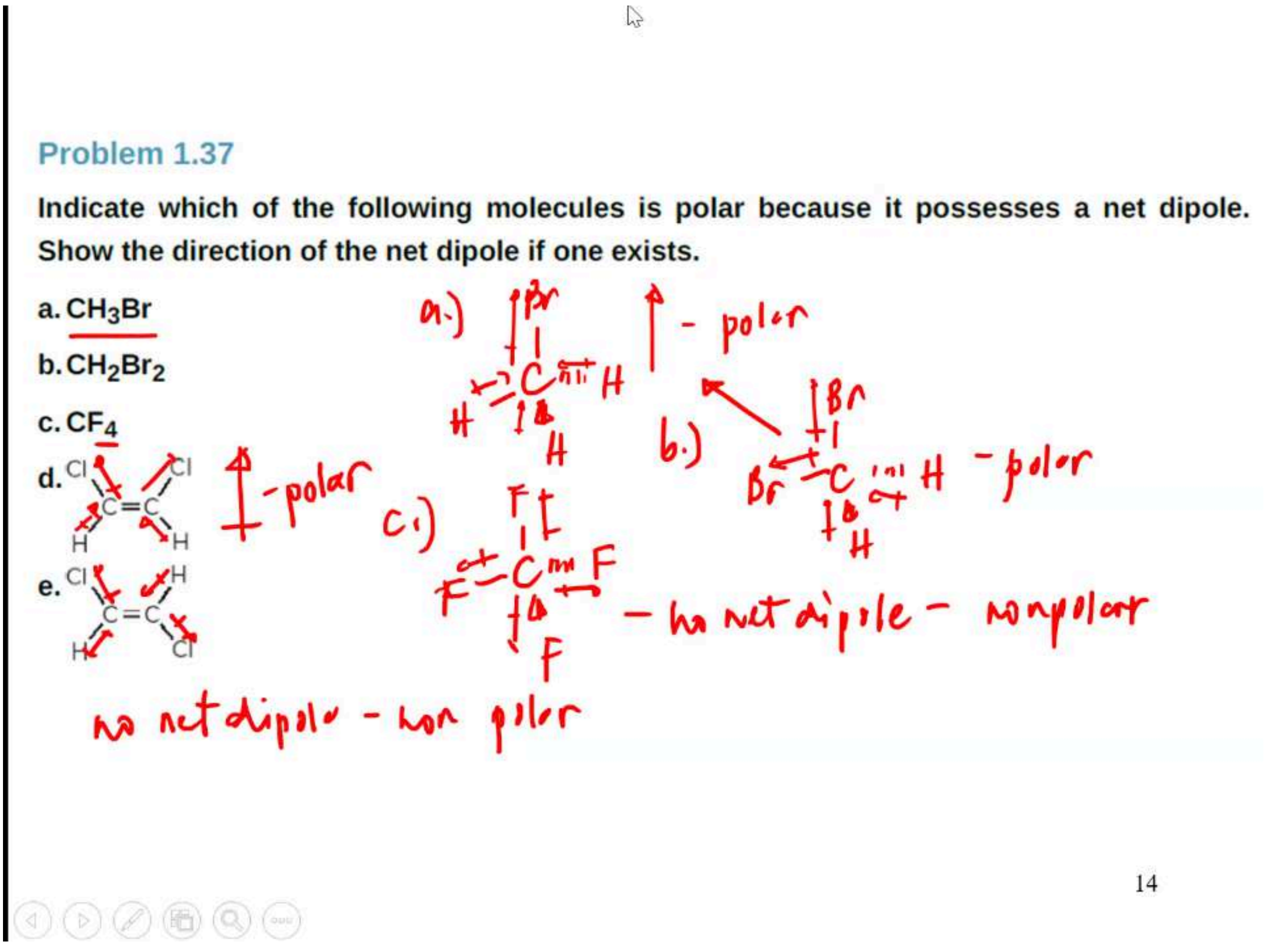


The net dipole bisects the H−O−H bond angle.
The two individual dipoles reinforce.

H_2O is a polar molecule.


a. Color scheme used for electron density

b. Electrostatic potential plot



Problem 1.37

Indicate which of the following molecules is polar because it possesses a net dipole. Show the direction of the net dipole if one exists.

a. CH_3Br

b. CH_2Br_2

c. CF_4

d.

e.

a.) ↑ - polar

b.) - polar

c.) - no net dipole - nonpolar

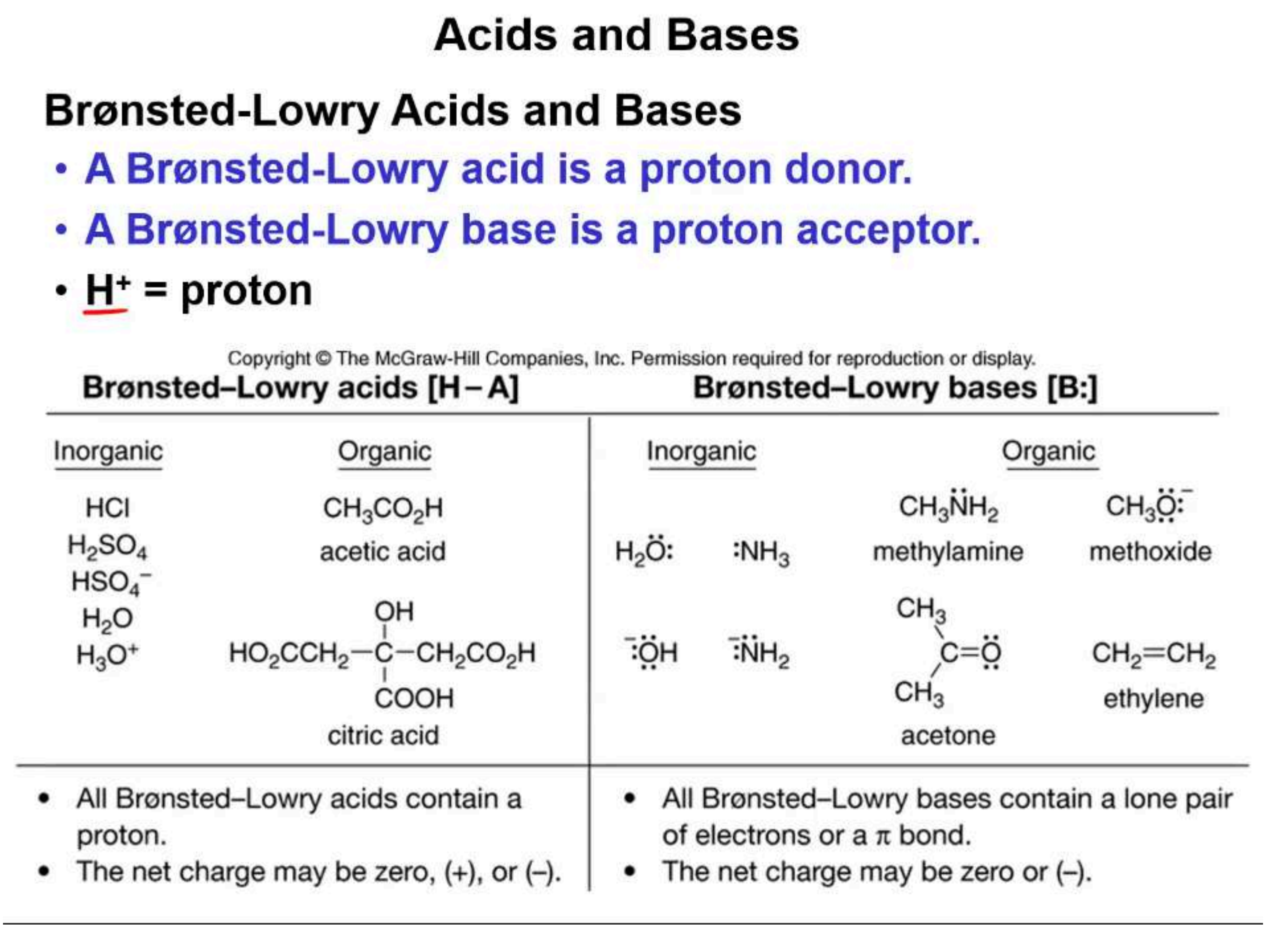
d. ↑ - polar

e. no net dipole - non polar

Bronsted Lowry Acids and Bases

- bronsted lowry acid is a proton donor
- bronsted lowry base is a proton acceptor

- H^+ = proton

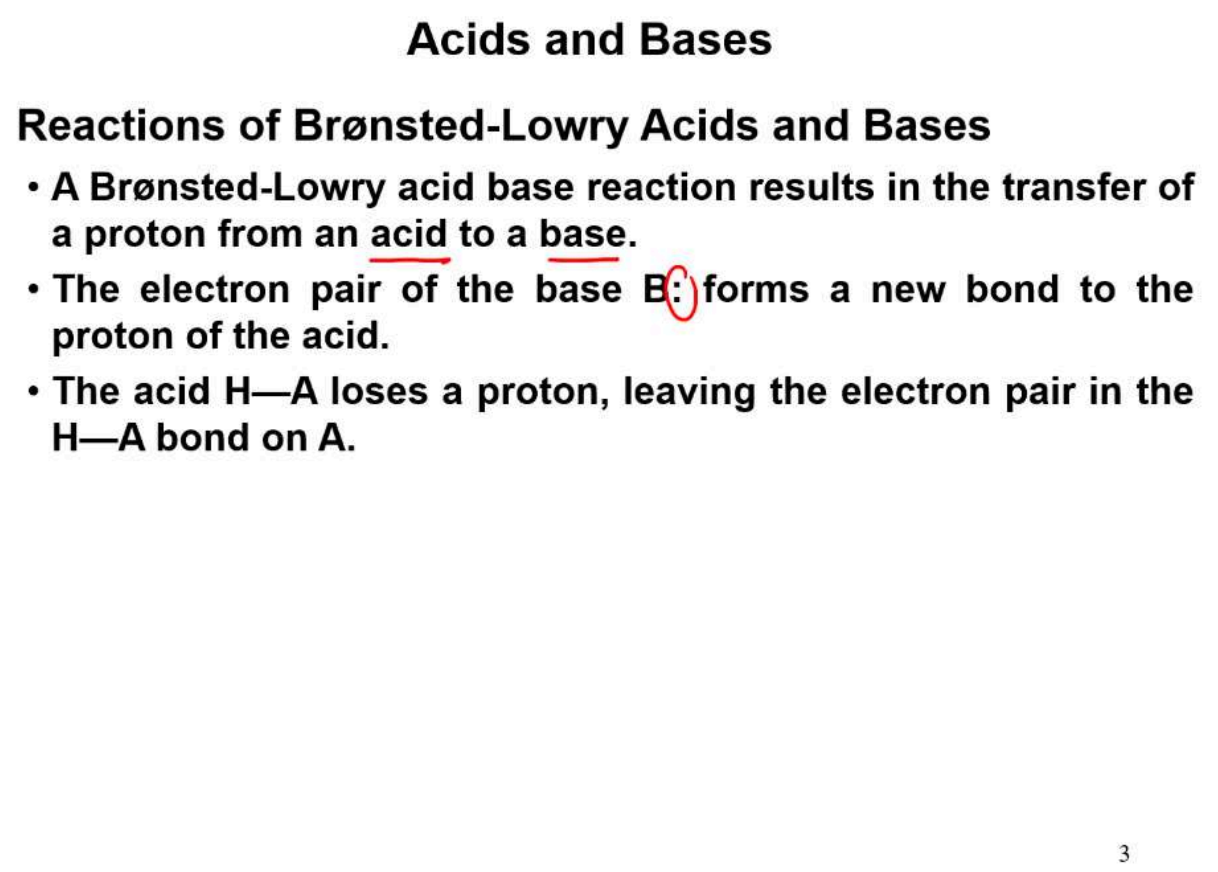


Acids and Bases

Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid is a proton donor.
- A Brønsted-Lowry base is a proton acceptor.
- H^+ = proton

Brønsted–Lowry acids [H–A]		**Brønsted–Lowry bases [B:]**			
Inorganic	Organic	Inorganic		Organic	
HCl H_2SO_4 HSO_4^- H_2O H_3O^+	CH_3CO_2H acetic acid	$H_2\ddot{O}:$	$:NH_3$	$CH_3\ddot{N}H_2$ methylamine	$CH_3\ddot{\underset{..}{O}}:^-$ methoxide
	$HO_2CCH_2-\overset{OH}{\underset{COOH}{C}}-CH_2CO_2H$ citric acid	$^-:\ddot{\underset{..}{O}}H$	$^-:\ddot{N}H_2$	$(CH_3)_2C=\ddot{\underset{..}{O}}$ acetone	$CH_2=CH_2$ ethylene
• All Brønsted–Lowry acids contain a proton. • The net charge may be zero, (+), or (–).		• All Brønsted–Lowry bases contain a lone pair of electrons or a π bond. • The net charge may be zero or (–).			

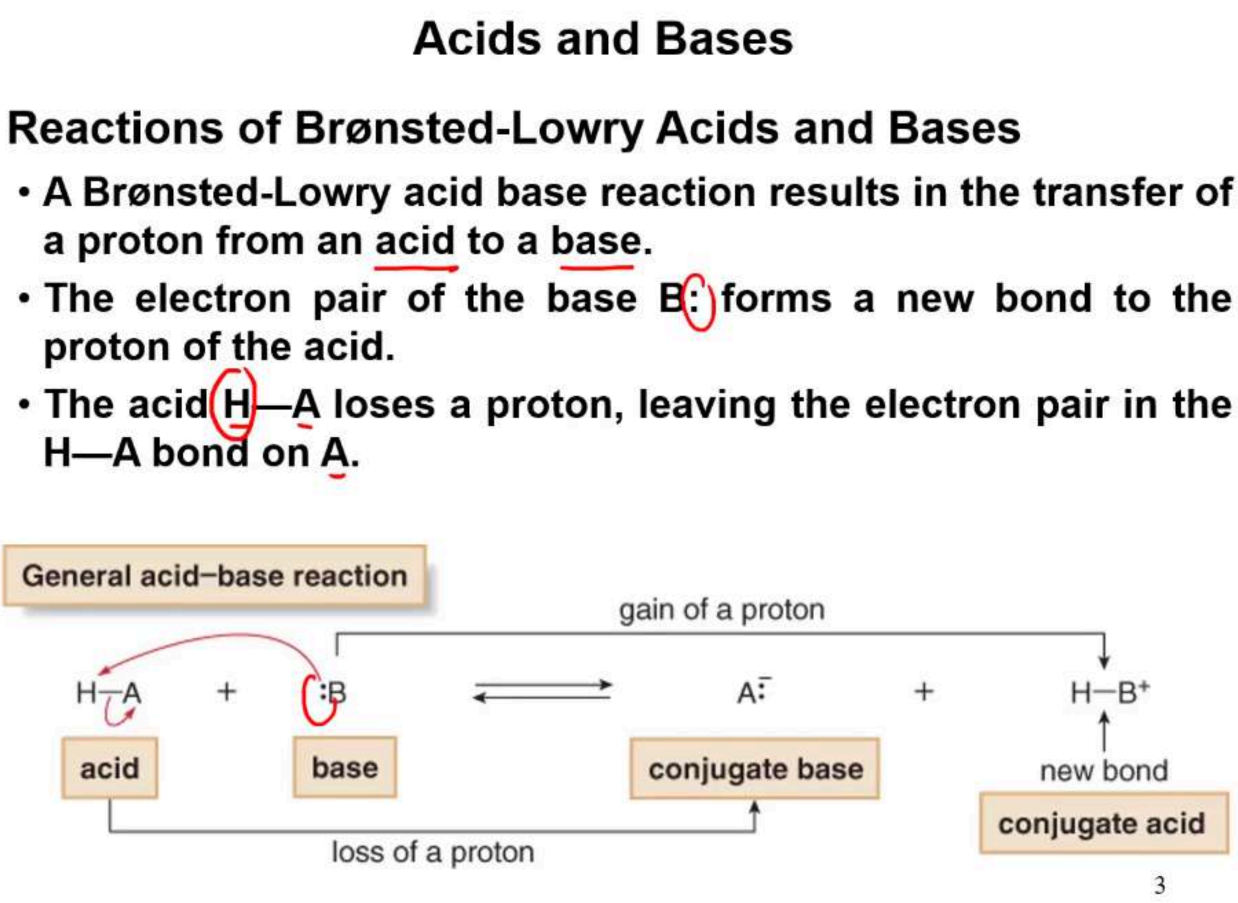


Acids and Bases

Reactions of Brønsted-Lowry Acids and Bases

- A Brønsted-Lowry acid base reaction results in the transfer of a proton from an acid to a base.
- The electron pair of the base B: forms a new bond to the proton of the acid.
- The acid H—A loses a proton, leaving the electron pair in the H—A bond on A.

Bronsted lowry acid base reactions results in the transfer of a proton from an acid to a base.



Acids and Bases

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- The electron pair of the base B: forms a new bond to the proton of the acid.
- The acid H—A loses a proton, leaving the electron pair in the H—A bond on A.

General acid−base reaction

$$H{-}A \; + \; :B \; \rightleftharpoons \; A:^{-} \; + \; H{-}B^{+}$$

acid

base

conjugate base

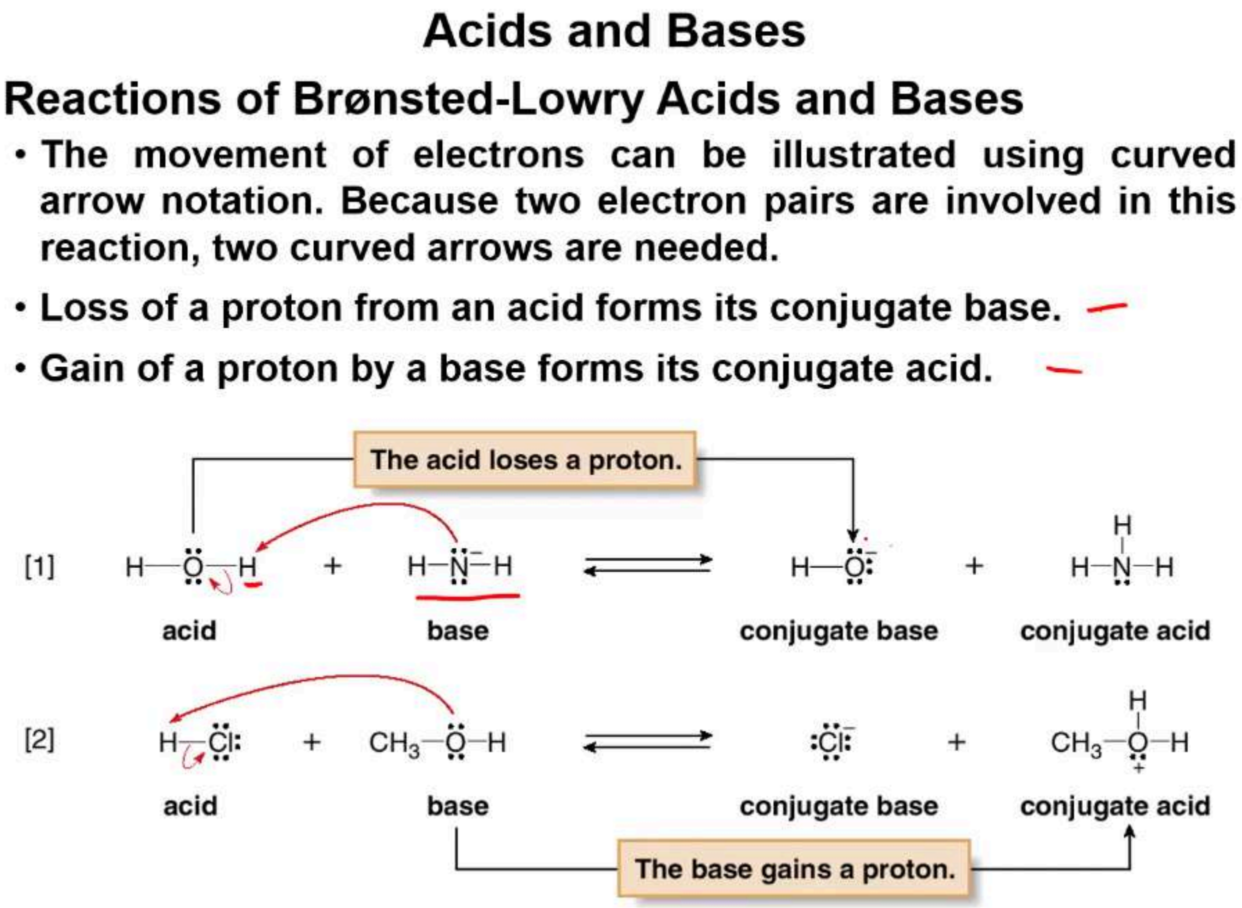
conjugate acid

gain of a proton

loss of a proton

new bond

Reactions of Bronsted Lowry Acids and Bases



Acids and Bases

Reactions of Brønsted-Lowry Acids and Bases

- The movement of electrons can be illustrated using curved arrow notation. Because two electron pairs are involved in this reaction, two curved arrows are needed.
- Loss of a proton from an acid forms its conjugate base.
- Gain of a proton by a base forms its conjugate acid.

Acid Strength and pK_a

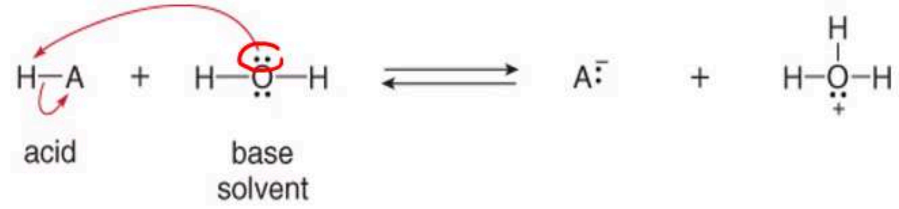
Acid strength is the tendency of an acid to donate a proton.
The more readily a compound donate a proton, the stronger an acid it is.
Acidity is measured by an equilibrium constant.

Acids and Bases

Acid Strength and pK_a

- **Acid strength is the tendency of an acid to donate a proton.**
- **The more readily a compound donates a proton, the stronger an acid it is.**
- **Acidity is measured by an equilibrium constant.**

Dissolving an acid in water



Equilibrium constant

$$K_{eq} = \frac{[\text{products}]}{[\text{starting materials}]} = \frac{[H_3O^+][A:^-]}{[H–A][H_2O]}$$

Any pure solid or liquid is omitted from the equation

Acids and Bases

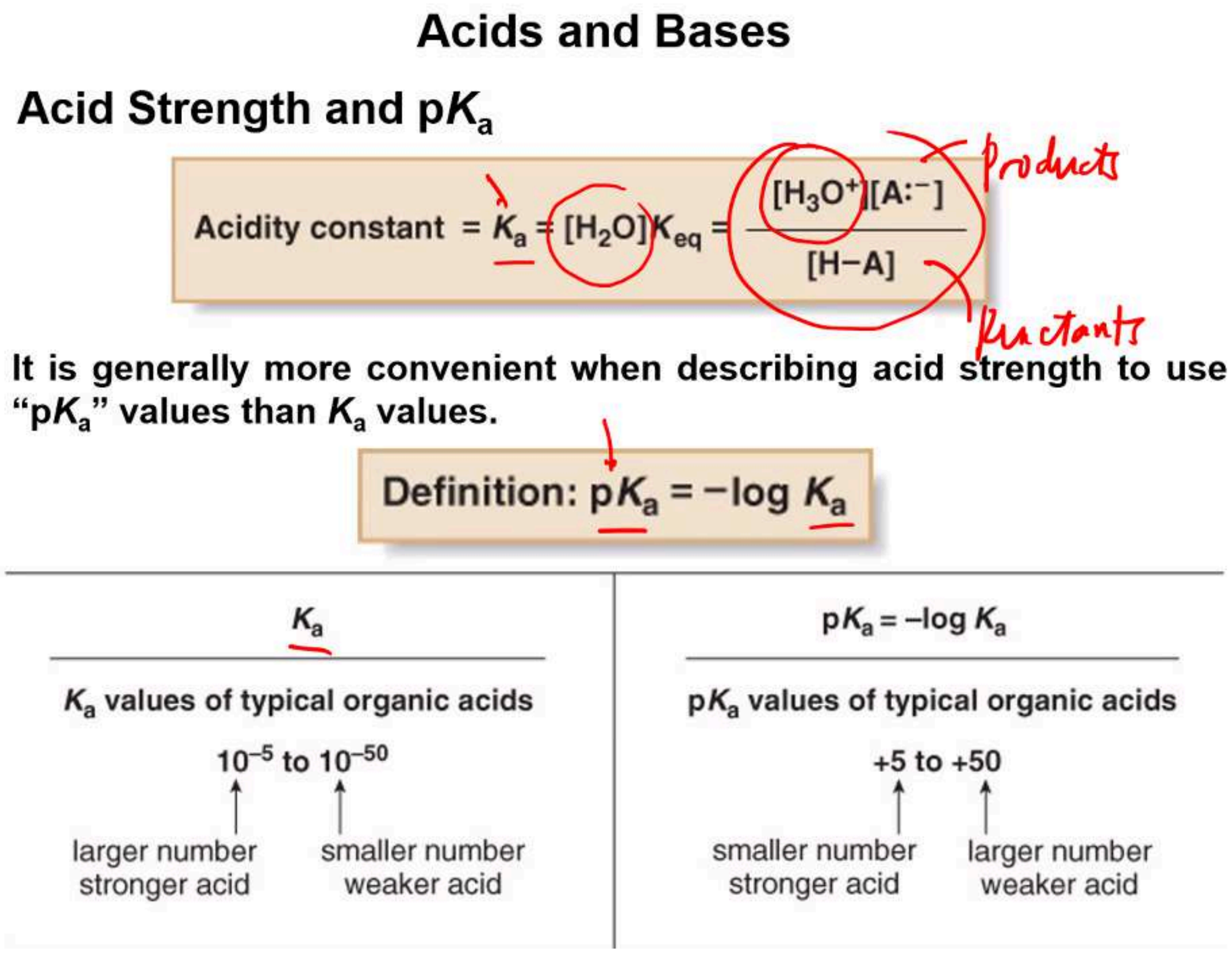
Acid Strength and pK_a

Acidity constant $= K_a = [H_2O]K_{eq} = \dfrac{[H_3O^+][A:^-]}{[H–A]}$

Definition: p$K_a = -\log K_a$

The value of K_a will tell you the direction. If K_a is high, it tends to the product, if K_a is low, then it tends to the reactants.

pK_a is a more convenient scale.



Acids and Bases

Acid Strength and pK_a

$$\text{Acidity constant} = K_a = [H_2O]K_{eq} = \frac{[H_3O^+][A:^-]}{[H-A]}$$

Products

Reactants

It is generally more convenient when describing acid strength to use "pK_a" values than K_a values.

Definition: pK_a = −log K_a

K_a	pK_a = −log K_a
K_a values of typical organic acids	pK_a values of typical organic acids
10^{-5} to 10^{-50}	+5 to +50
↑ larger number stronger acid	↑ smaller number stronger acid
↑ smaller number weaker acid	↑ larger number weaker acid

PKA = stronger is smaller
KA = stronger is larger

Acids and Bases

Acid Strength and pK_a

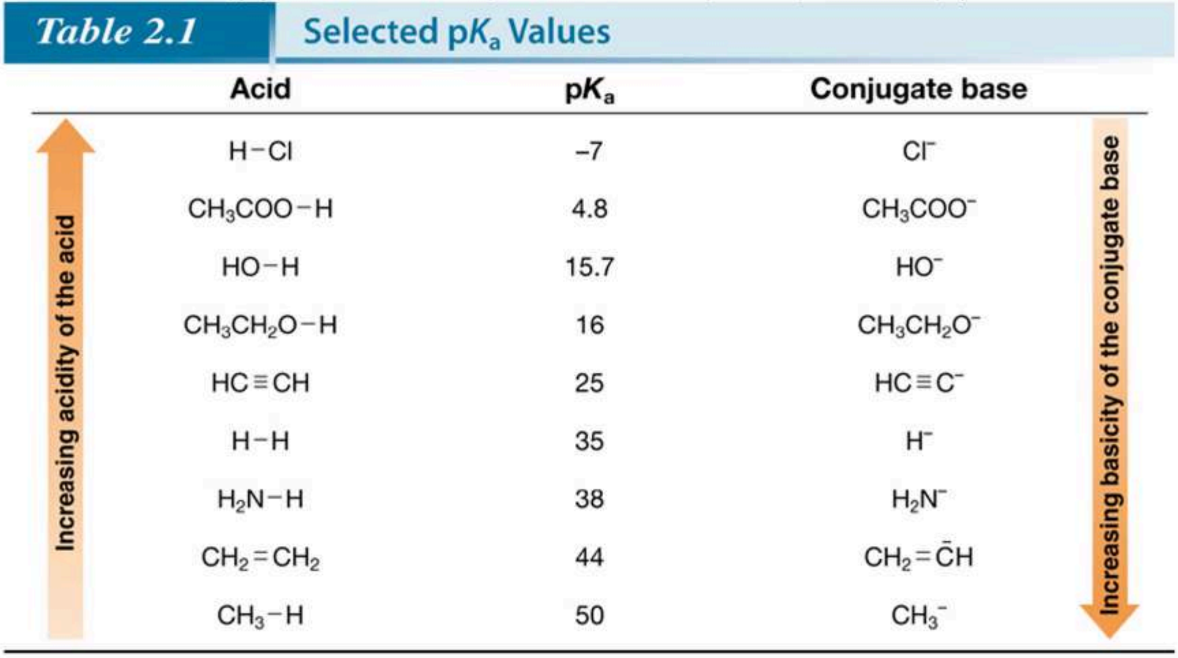
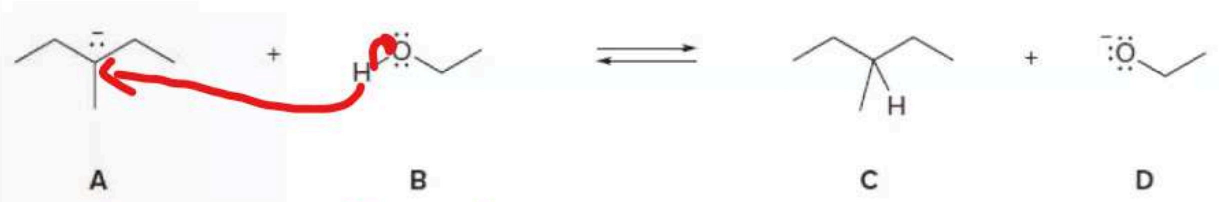


Table 2.1 Selected pK_a Values

Acid	pK_a	Conjugate base
$H-Cl$	−7	Cl^-
CH_3COO-H	4.8	CH_3COO^-
$HO-H$	15.7	HO^-
CH_3CH_2O-H	16	$CH_3CH_2O^-$
$HC\equiv CH$	25	$HC\equiv C^-$
$H-H$	35	H^-
H_2N-H	38	H_2N^-
$CH_2=CH_2$	44	$CH_2=\bar{C}H$
CH_3-H	50	CH_3^-

![[]]

Label the acid and base, and the conjugate acid and base, in the following reaction. Use curved arrow notation to show the movement of electron pairs.

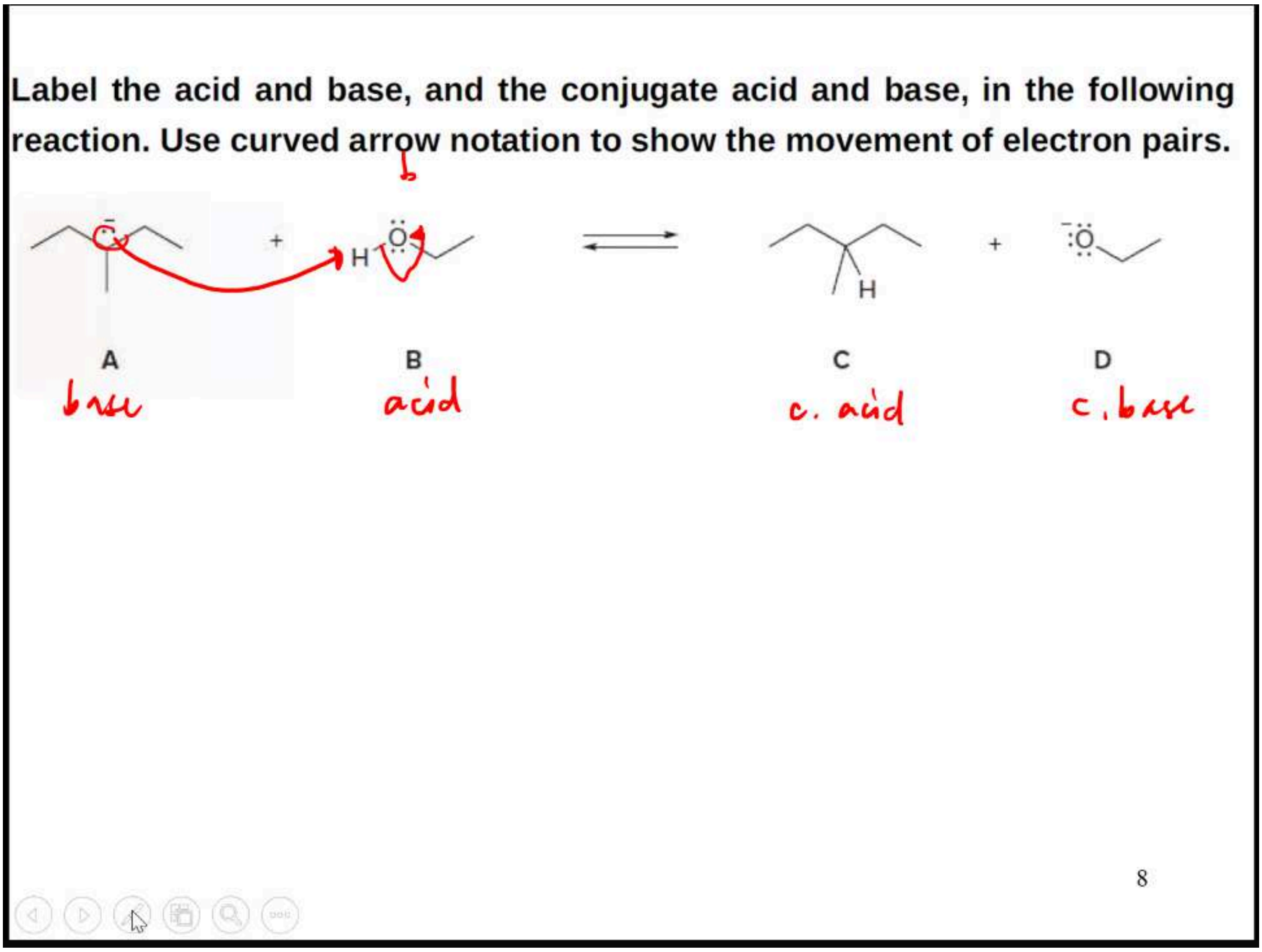


base

acid

acid
conj

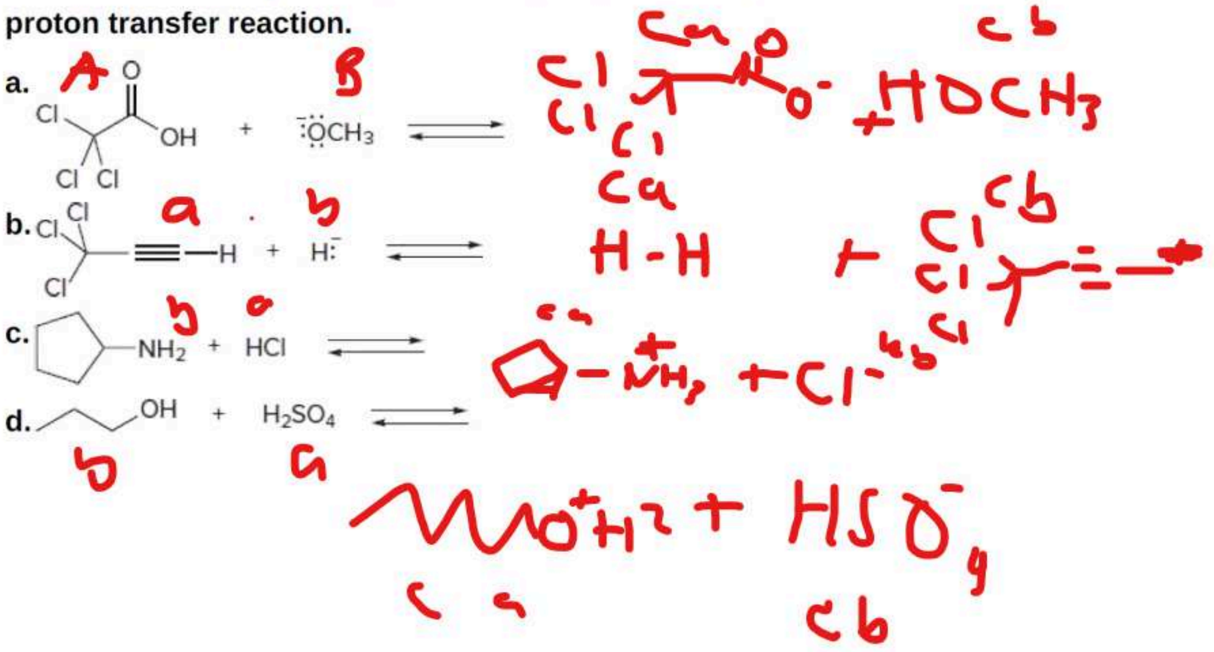
base
conj



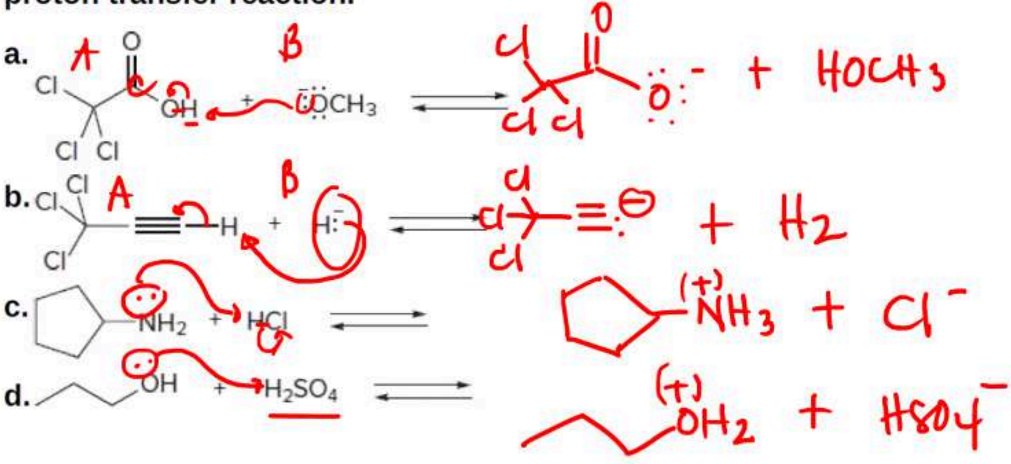
Label the acid and base, and the conjugate acid and base, in the following reaction. Use curved arrow notation to show the movement of electron pairs.

electrons to atoms arrow direction

Decide which compound is the acid and which is the base, and draw the products of each proton transfer reaction.



Decide which compound is the acid and which is the base, and draw the products of each proton transfer reaction.

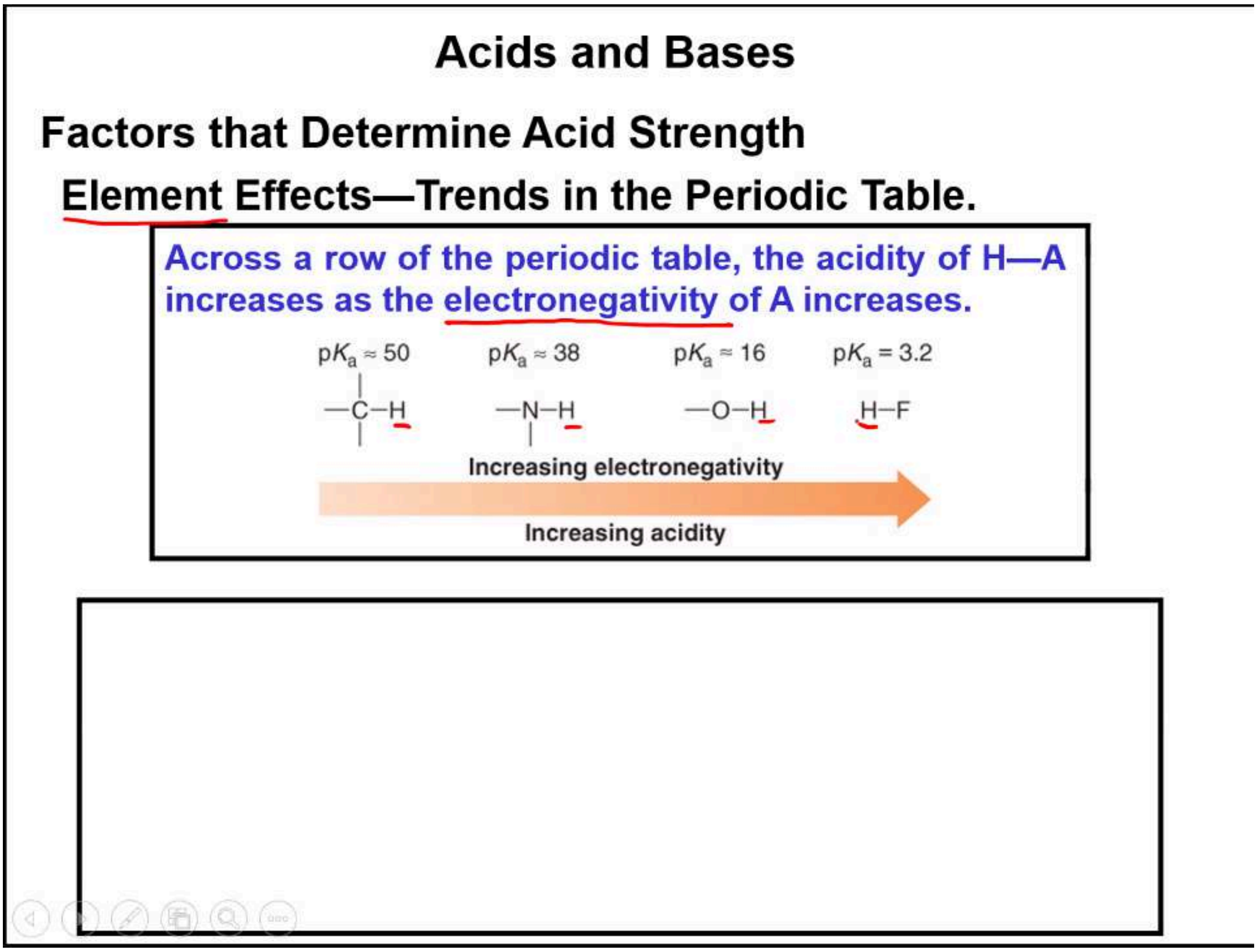


Factors that Determine Acid Strength

H-A = acid
A- = base

- Anything that stabilizes a conjugate base A- makes the starting acid HA more acidic
- If the acid is able to donate its proton and it leaves it with a stable conjugate base, It can give away its proton with ease and thats what makes it acidic.
- Four factorsa ffect the acidity of H-A these are:
  - Element effects - the most
  - Inductive effects
  - Resonance effects
  - Hybridization effects

Element effects- trends in the periodic table



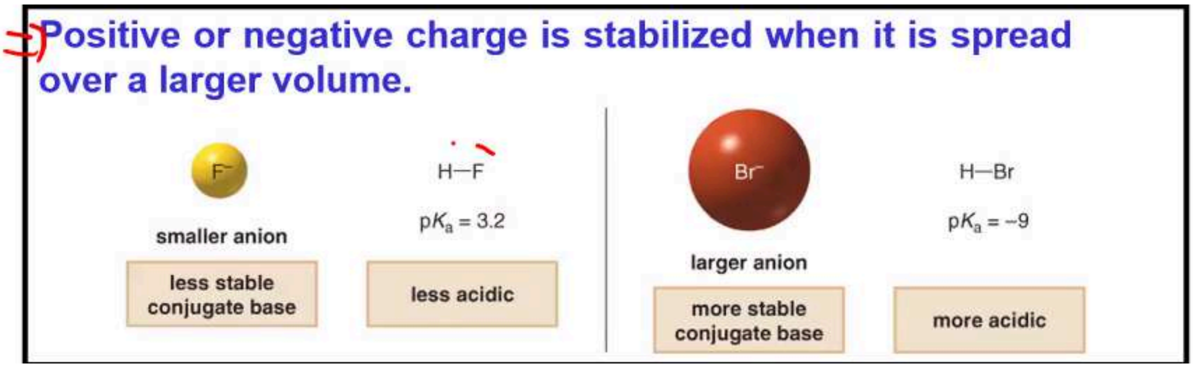
Acids and Bases

Factors that Determine Acid Strength

Element Effects—Trends in the Periodic Table.

Across a row of the periodic table, the acidity of H—A increases as the electronegativity of A increases.

Increasing electronegativity- increasing acidity



=) **Positive or negative charge is stabilized when it is spread over a larger volume.**

F^-	H—F	Br^-	H—Br
smaller anion	$pK_a = 3.2$	larger anion	$pK_a = -9$
less stable conjugate base	less acidic	more stable conjugate base	more acidic

it is spread

$HF <<< HCl < HBr < HI$

Acids and Bases

Factors that Determine Acid Strength

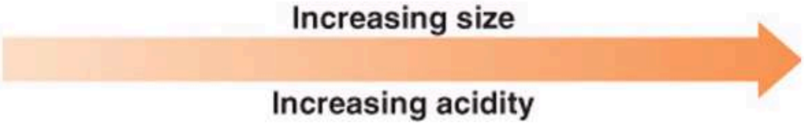
Element Effects—Trends in the Periodic Table.

- **Down a column of the periodic table, the acidity of H—A increases as the size of A increases.**

$\underline{pK_a = 3.2}$ $\qquad$ $\underline{pK_a = -7}$ $\qquad$ $pK_a = -9$ $\qquad$ $pK_a = -10$

$H{-}F \ll < H{-}Cl < H{-}Br < H{-}I$

Increasing size



Increasing acidity

Acids and Bases

Factors that Determine Acid Strength

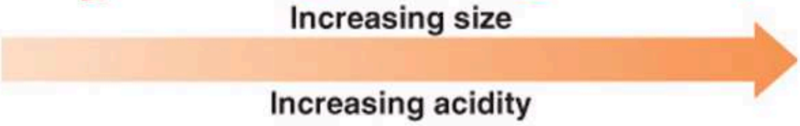
Element Effects—Trends in the Periodic Table.

- **Down a column of the periodic table, the acidity of H—A increases as the size of A increases.**

$\underline{pK_a = 3.2}$ $\qquad$ $\underline{pK_a = -7}$ $\qquad$ $pK_a = -9$ $\qquad$ $pK_a = -10$

$H{-}\underset{=}{F} \ll < H{-}\underset{=}{Cl} < H{-}\underset{=}{Br} < H{-}\underset{=}{I}$

Increasing size

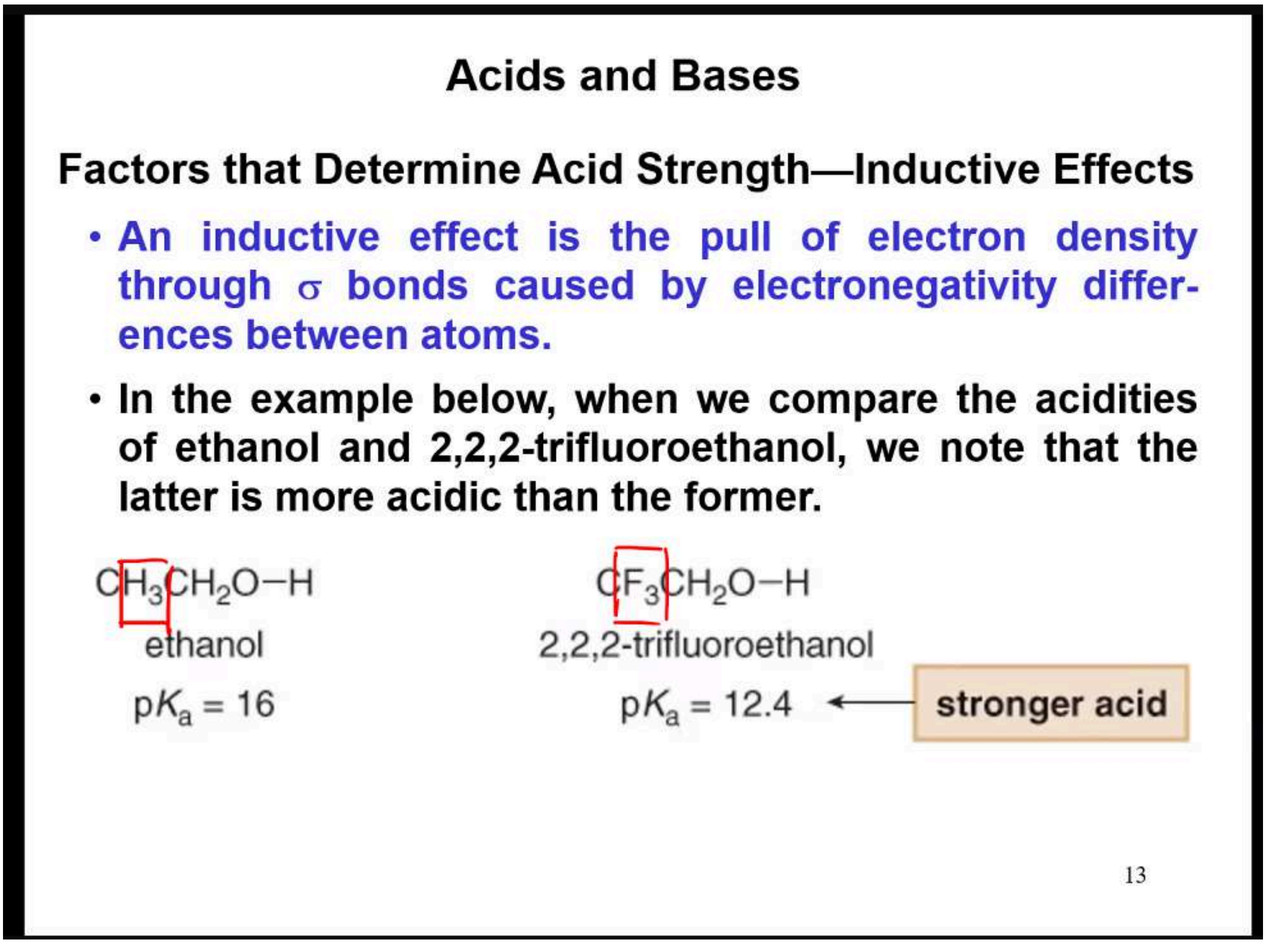


Increasing acidity

- **Size, and not electronegativity, determines acidity down a column.**
- * **The acidity of H—A increases both left-to-right across a row and down a column of the periodic table.**
- **Although four factors determine the overall acidity of a particular hydrogen atom, element effects—the identity of A—is the single most important factor in determining the acidity of the H—A bond.**

Inductive effects

- An inductive effect is the pull of electron density through σ bonds caused by electronegativity differences between two atoms.



Acids and Bases

Factors that Determine Acid Strength—Inductive Effects

- **An inductive effect is the pull of electron density through σ bonds caused by electronegativity differences between atoms.**
- **In the example below, when we compare the acidities of ethanol and 2,2,2-trifluoroethanol, we note that the latter is more acidic than the former.**

$CH_3CH_2O{-}H$

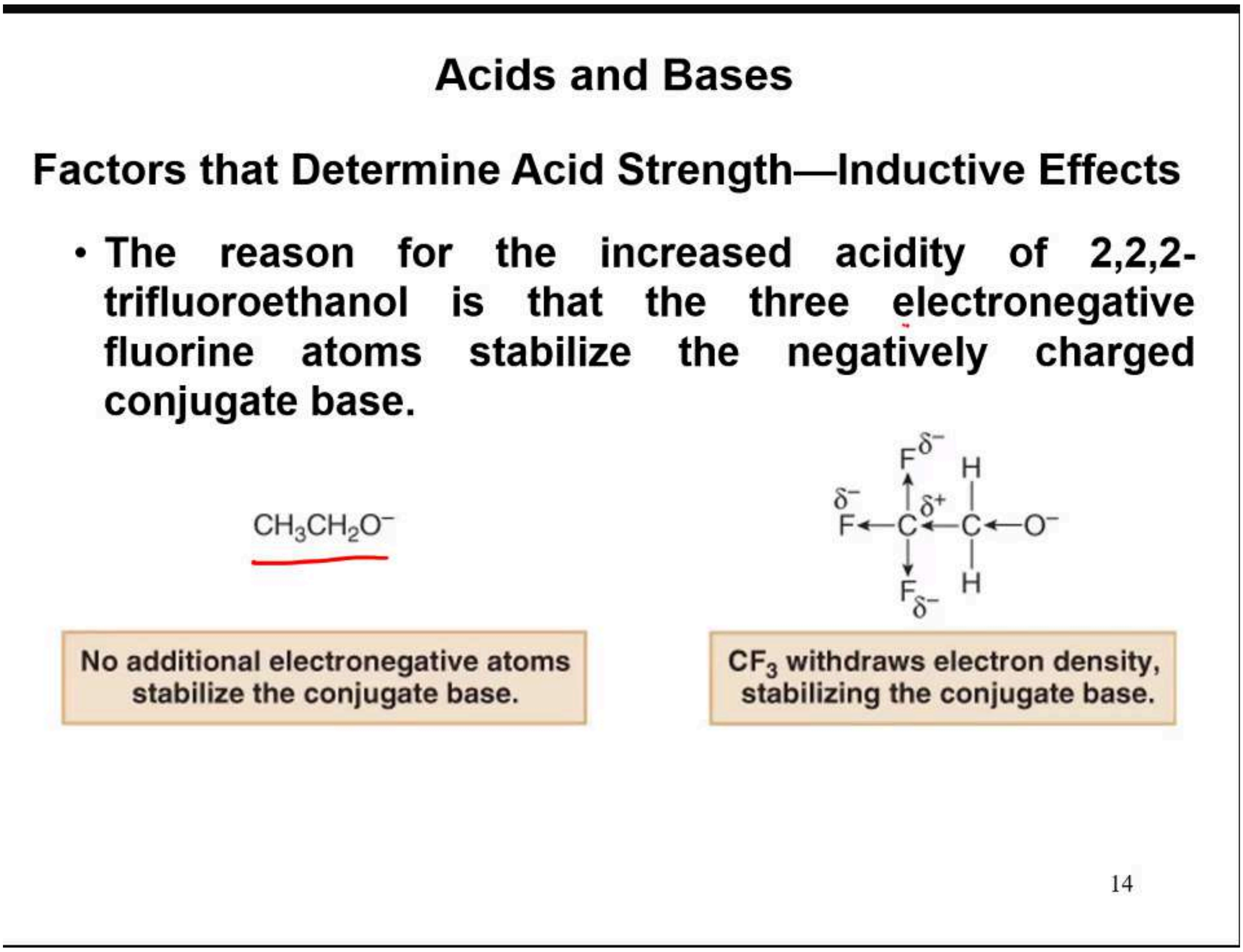
ethanol

$pK_a = 16$

$CF_3CH_2O{-}H$

2,2,2-trifluoroethanol

$pK_a = 12.4$ ← **stronger acid**



Acids and Bases

Factors that Determine Acid Strength—Inductive Effects

- **The reason for the increased acidity of 2,2,2-trifluoroethanol is that the three electronegative fluorine atoms stabilize the negatively charged conjugate base.**

$CH_3CH_2O^-$

No additional electronegative atoms stabilize the conjugate base.

CF_3 withdraws electron density, stabilizing the conjugate base.

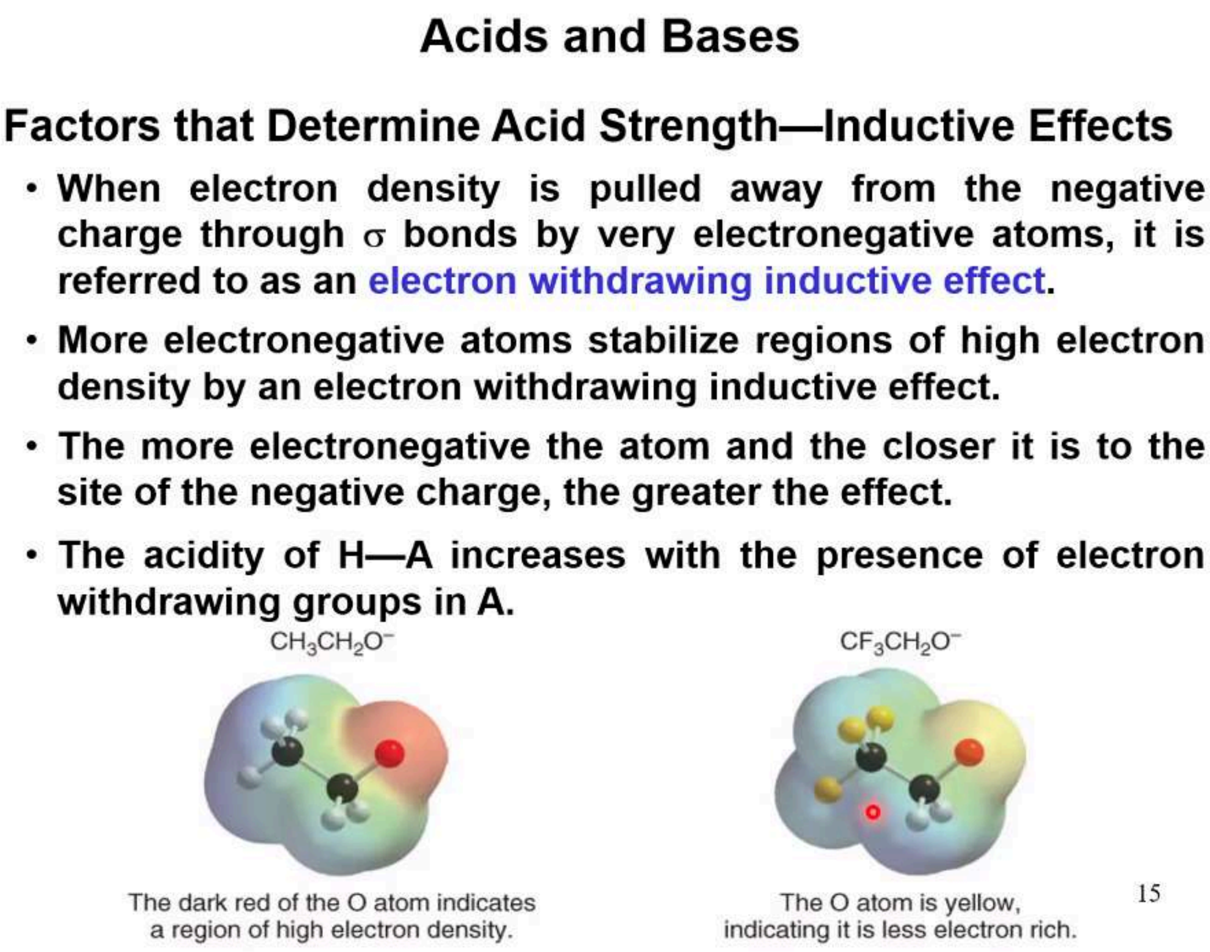
Electronegative fluorine draws electrons to it, withdrawing electron density stabilizing the conjugate base.

for CH3CH2O, no electronegative atoms to stabilize the conjugate base.

When electron density is pulled away from the negative charge through σ bonds by very electronegative atoms, it is referred to as an electron withdrawing inductive effect.

More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.

The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.



Acids and Bases

Factors that Determine Acid Strength—Inductive Effects

- **When electron density is pulled away from the negative charge through σ bonds by very electronegative atoms, it is referred to as an electron withdrawing inductive effect.**
- **More electronegative atoms stabilize regions of high electron density by an electron withdrawing inductive effect.**
- **The more electronegative the atom and the closer it is to the site of the negative charge, the greater the effect.**
- **The acidity of H—A increases with the presence of electron withdrawing groups in A.**

$CH_3CH_2O^-$

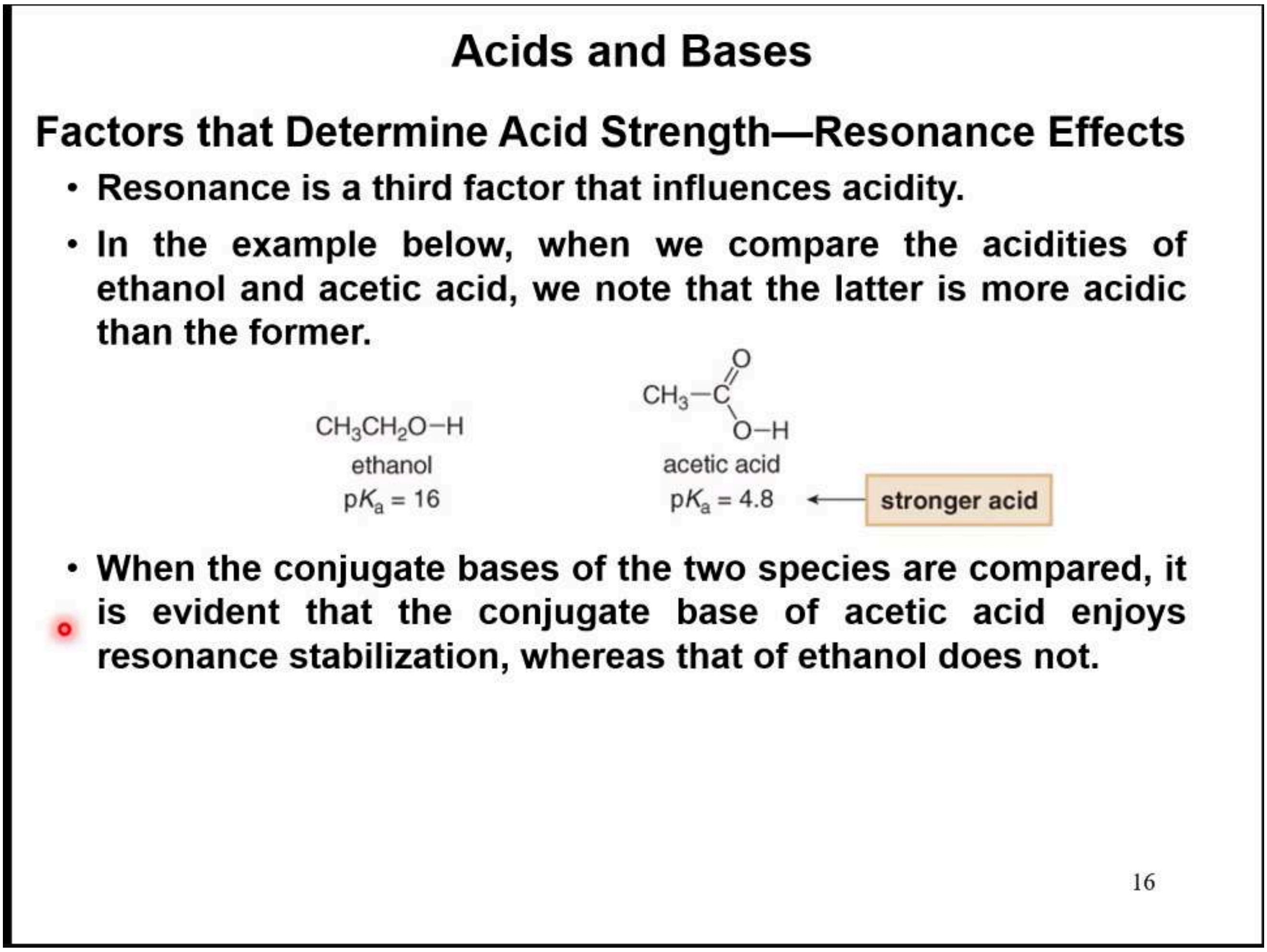
The dark red of the O atom indicates a region of high electron density.

$CF_3CH_2O^-$

The O atom is yellow, indicating it is less electron rich.

Resonance Effects

Resonance is a third factor that influences acidity.
Resonance stabilized



Acids and Bases

Factors that Determine Acid Strength—Resonance Effects

- **Resonance is a third factor that influences acidity.**
- **In the example below, when we compare the acidities of ethanol and acetic acid, we note that the latter is more acidic than the former.**

$CH_3CH_2O{-}H$

ethanol

$pK_a = 16$

$CH_3{-}C({=}O){-}O{-}H$

acetic acid

$pK_a = 4.8$ ← stronger acid

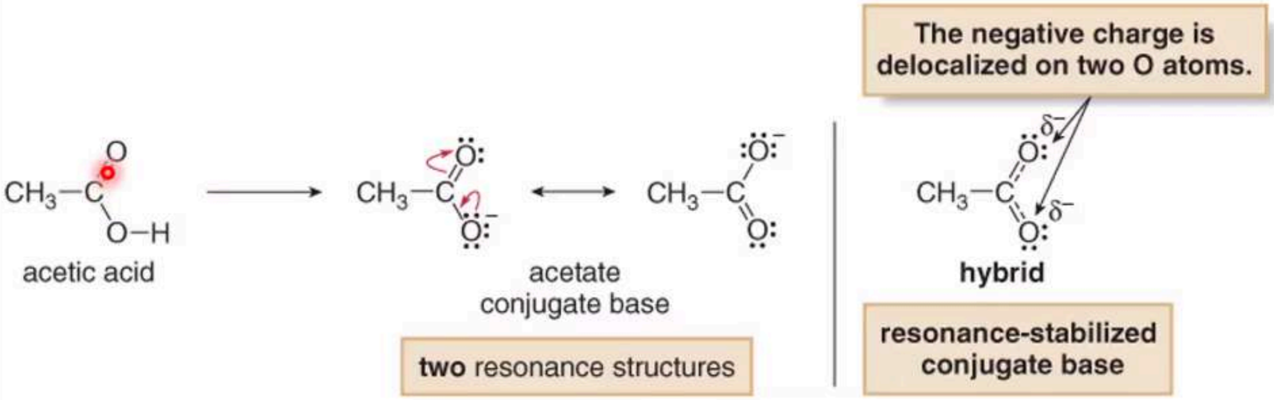
- **When the conjugate bases of the two species are compared, it is evident that the conjugate base of acetic acid enjoys resonance stabilization, whereas that of ethanol does not.**

ethoxide is not stable

Acids and Bases

Factors that Affects Acid Strength—Resonance Effects

- **Resonance delocalization makes CH_3COO^- more stable than $CH_3CH_2O^-$, so CH_3COOH is a stronger acid than CH_3CH_2OH.**

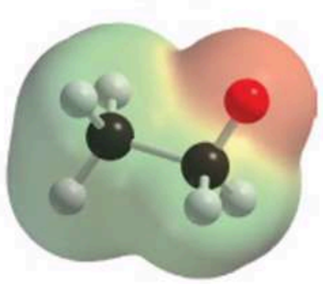


Acids and Bases

Factors that Determine Acid Strength—Resonance Effects

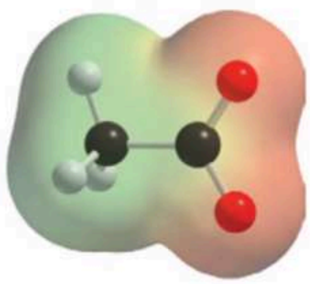
- **Electrostatic potential plots of $CH_3CH_2O^-$ and CH_3COO^- below indicate that the negative charge is concentrated on a single O in $CH_3CH_2O^-$, but delocalized over both of the O atoms in CH_3COO^-.**

$CH_3CH_2O^-$



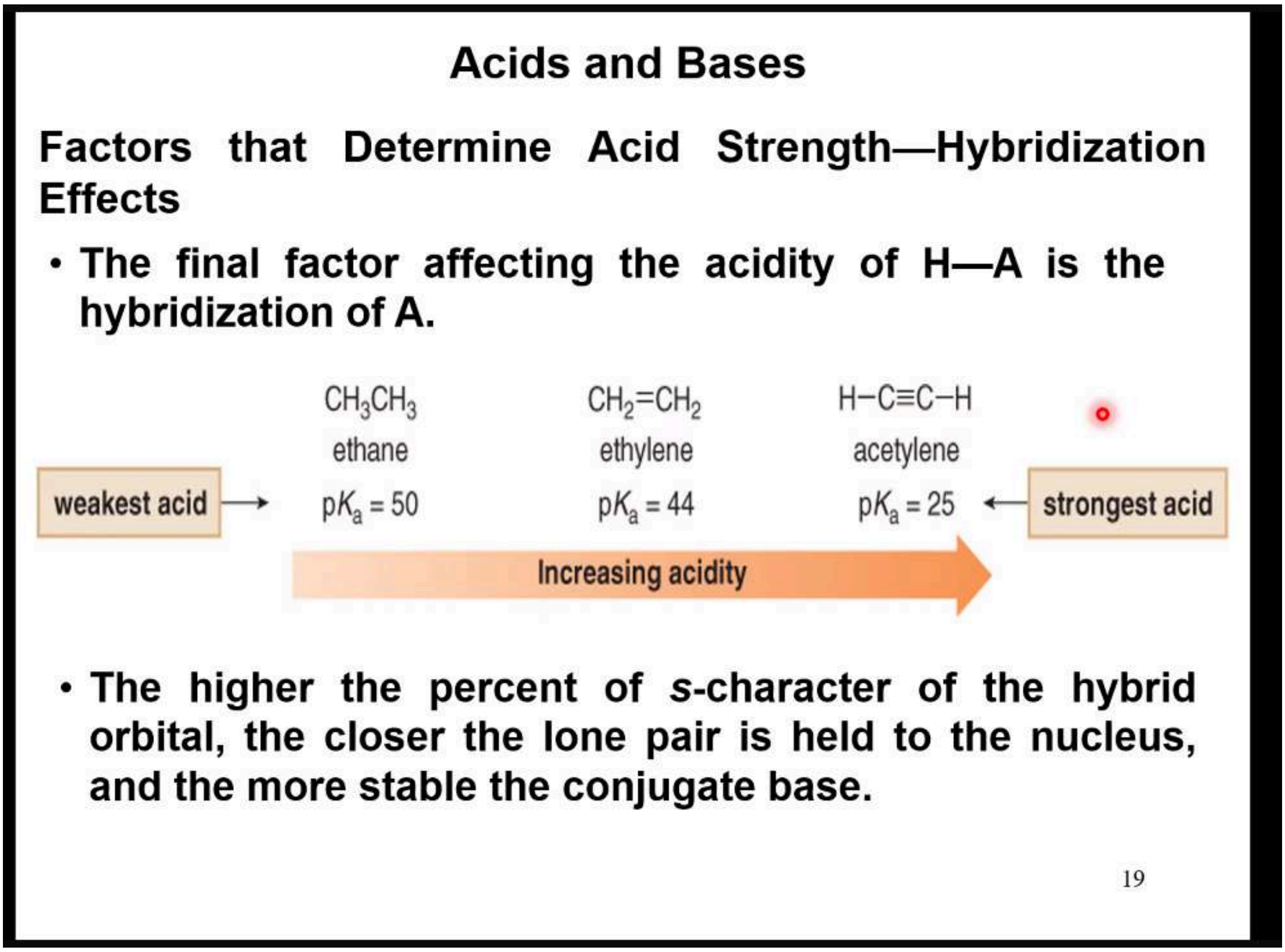
The negative charge is concentrated on the single oxygen atom, making this anion *less stable.*

CH_3COO^-



The negative charge is delocalized over both oxygen atoms, making this anion *more stable.*

Hybridization Effects



Acids and Bases

Factors that Determine Acid Strength—Hybridization Effects

- The final factor affecting the acidity of H—A is the hybridization of A.

weakest acid →

CH_3CH_3
ethane
pK_a = 50

$CH_2{=}CH_2$
ethylene
pK_a = 44

H−C≡C−H
acetylene
pK_a = 25

← **strongest acid**

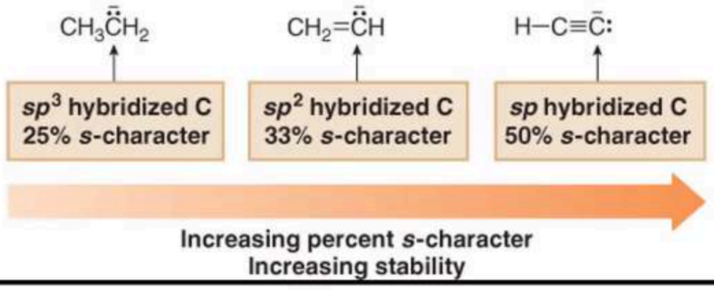
Increasing acidity

- The higher the percent of *s*-character of the hybrid orbital, the closer the lone pair is held to the nucleus, and the more stable the conjugate base.

Higher s character- stable base- stronger acid

Acids and Bases

Factors that Determine Acid Strength—Hybridization Effects



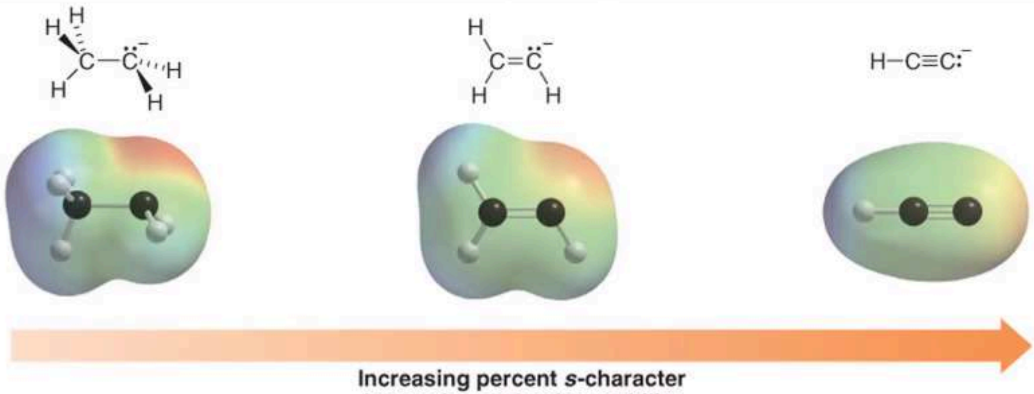
$CH_3\ddot{C}H_2^-$ | $CH_2{=}\ddot{C}H^-$ | $H{-}C{\equiv}C{:}^-$

***sp*^{3} hybridized C**
25% *s*-character

***sp*^{2} hybridized C**
33% *s*-character

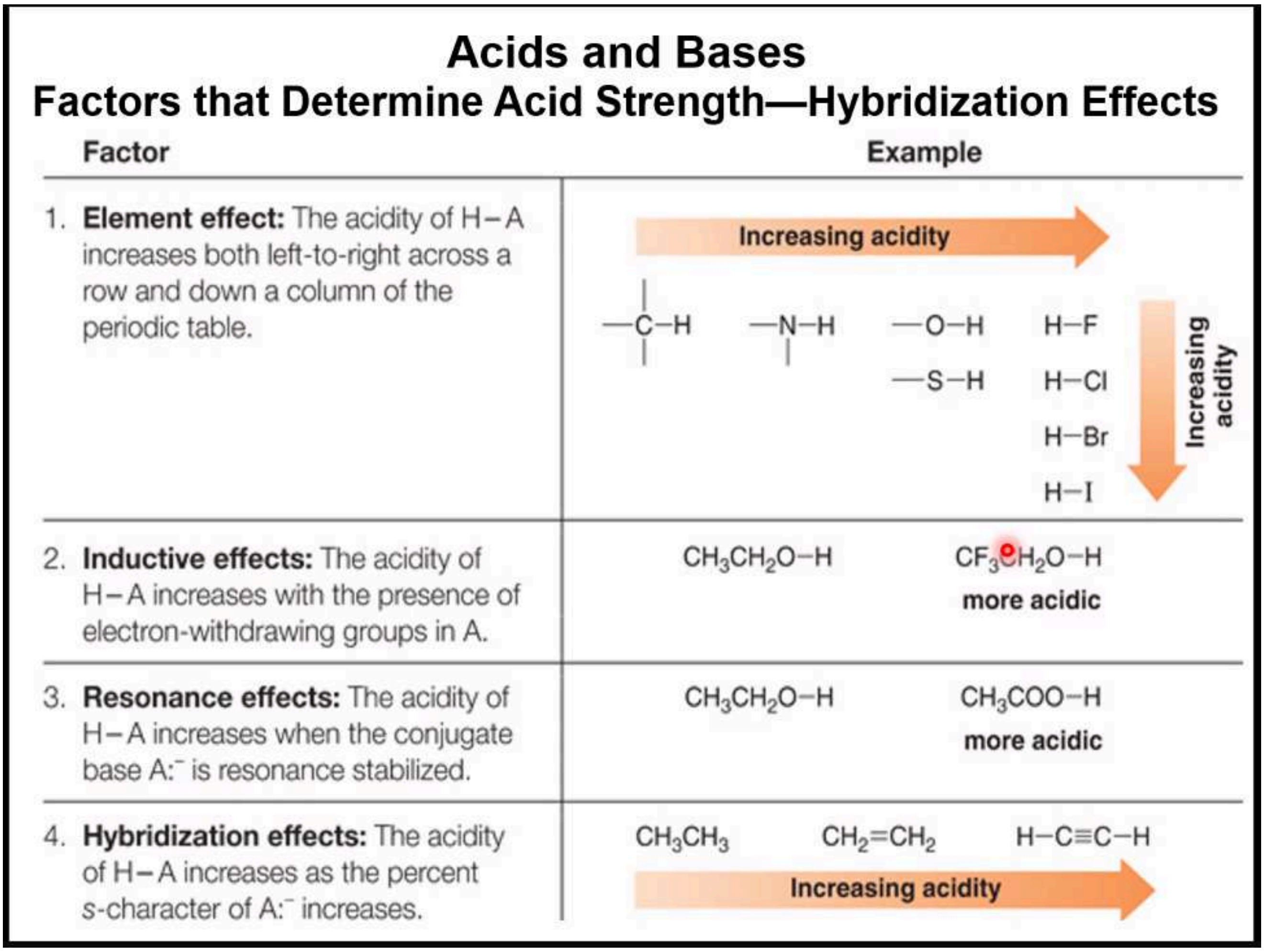
***sp* hybridized C**
50% *s*-character

Increasing percent *s*-character
Increasing stability



Increasing percent *s*-character
Increasing carbanion stability

- As the lone pair of electrons is pulled closer to the nucleus, the negatively charged carbon appears less intensely red.



Acids and Bases
Factors that Determine Acid Strength—Hybridization Effects

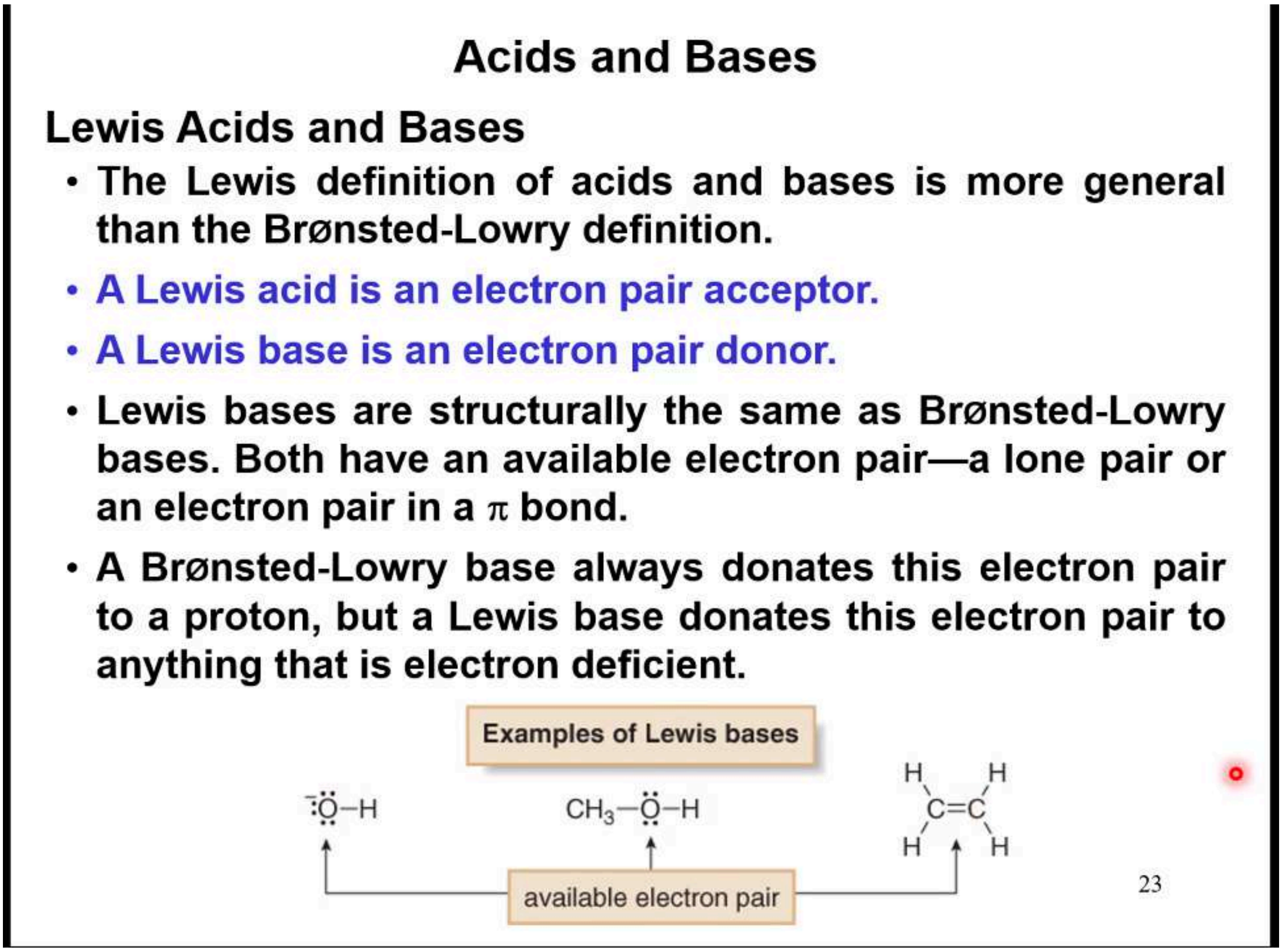
Factor	Example
1. **Element effect:** The acidity of H–A increases both left-to-right across a row and down a column of the periodic table.	Increasing acidity → —C—H —N—H —O—H H—F —S—H H—Cl H—Br H—I Increasing acidity ↓
2. **Inductive effects:** The acidity of H–A increases with the presence of electron-withdrawing groups in A.	$CH_3CH_2O{-}H$ $CF_3CH_2O{-}H$ more acidic
3. **Resonance effects:** The acidity of H–A increases when the conjugate base A:⁻ is resonance stabilized.	$CH_3CH_2O{-}H$ $CH_3COO{-}H$ more acidic
4. **Hybridization effects:** The acidity of H–A increases as the percent *s*-character of A:⁻ increases.	CH_3CH_3 $CH_2{=}CH_2$ $H{-}C{\equiv}C{-}H$ Increasing acidity →

commonly used bases in org chem
strong bases have weak conjugate acids, with pka values > 12
strong bases have a net negative charge, but not all negatively charged species are strong bases.
F- CL- BR- or I- are not strong bases
Carbanions, neg charge carbon are strong bases. butyllithium.
weaker org bases include triethylamine and pyridine.

Lewis Acids and Bases

Lewis definition of acids and bases is more general than the bronsted lowry definition
Lewis Bases donates electrons pair
Lewis Acids accepts electrons pair

Lewis bases are structurally the same as a bronsted lowry base. both have an available electron pair - alone pair or an electron pair in a π bond.



Acids and Bases

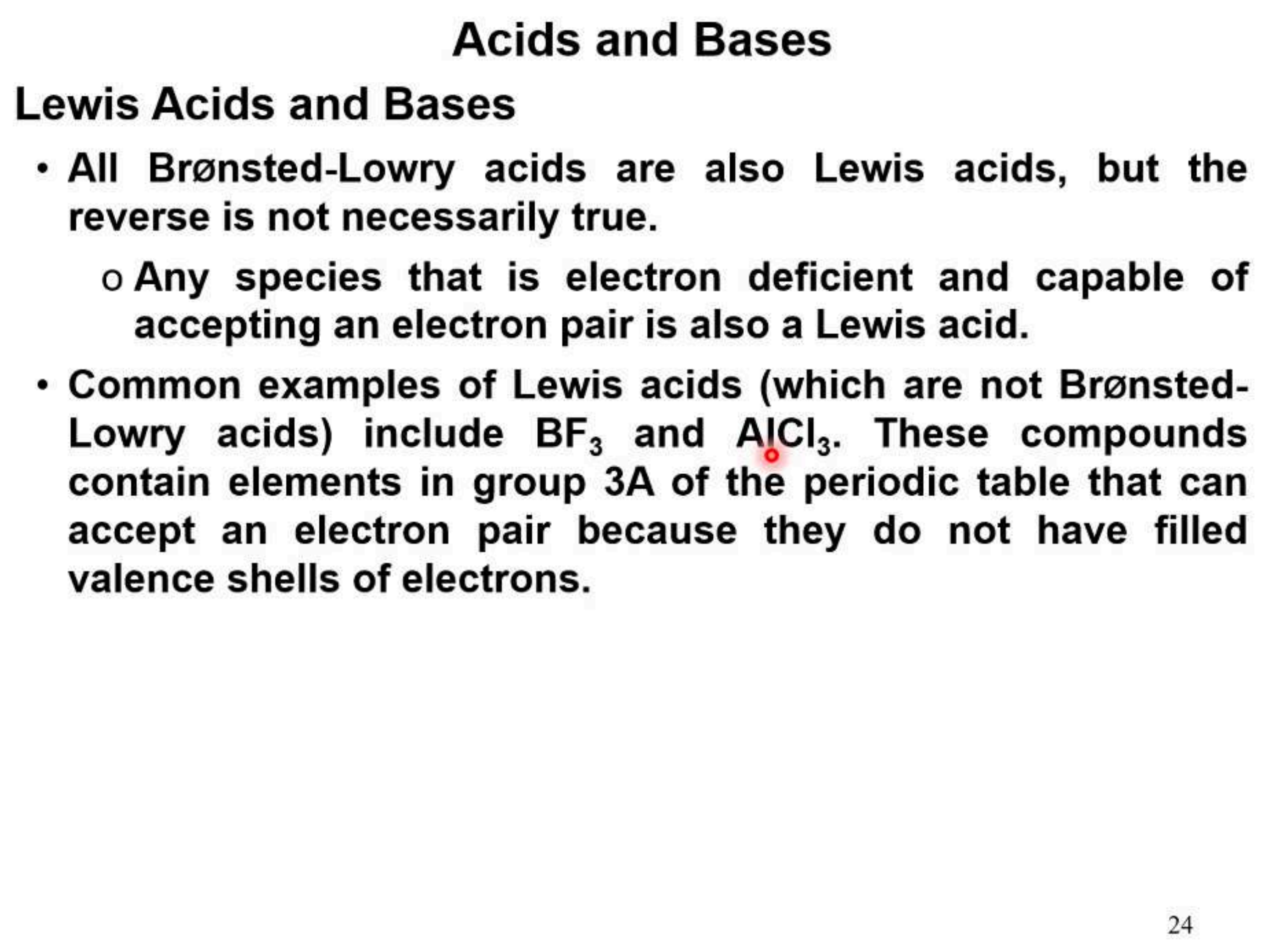
Lewis Acids and Bases

- The Lewis definition of acids and bases is more general than the Brønsted-Lowry definition.
- A Lewis acid is an electron pair acceptor.
- A Lewis base is an electron pair donor.
- Lewis bases are structurally the same as Brønsted-Lowry bases. Both have an available electron pair—a lone pair or an electron pair in a π bond.
- A Brønsted-Lowry base always donates this electron pair to a proton, but a Lewis base donates this electron pair to anything that is electron deficient.

Examples of Lewis bases

All bronsted lowry acids are lewis acids but the reverse is not true.

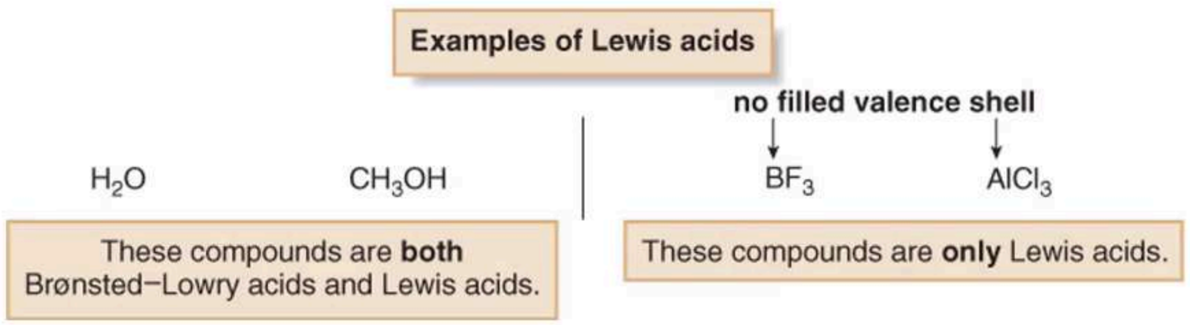
any species that is electron deficient and capable of accepting an electron pair is also a lewis acid.



Acids and Bases

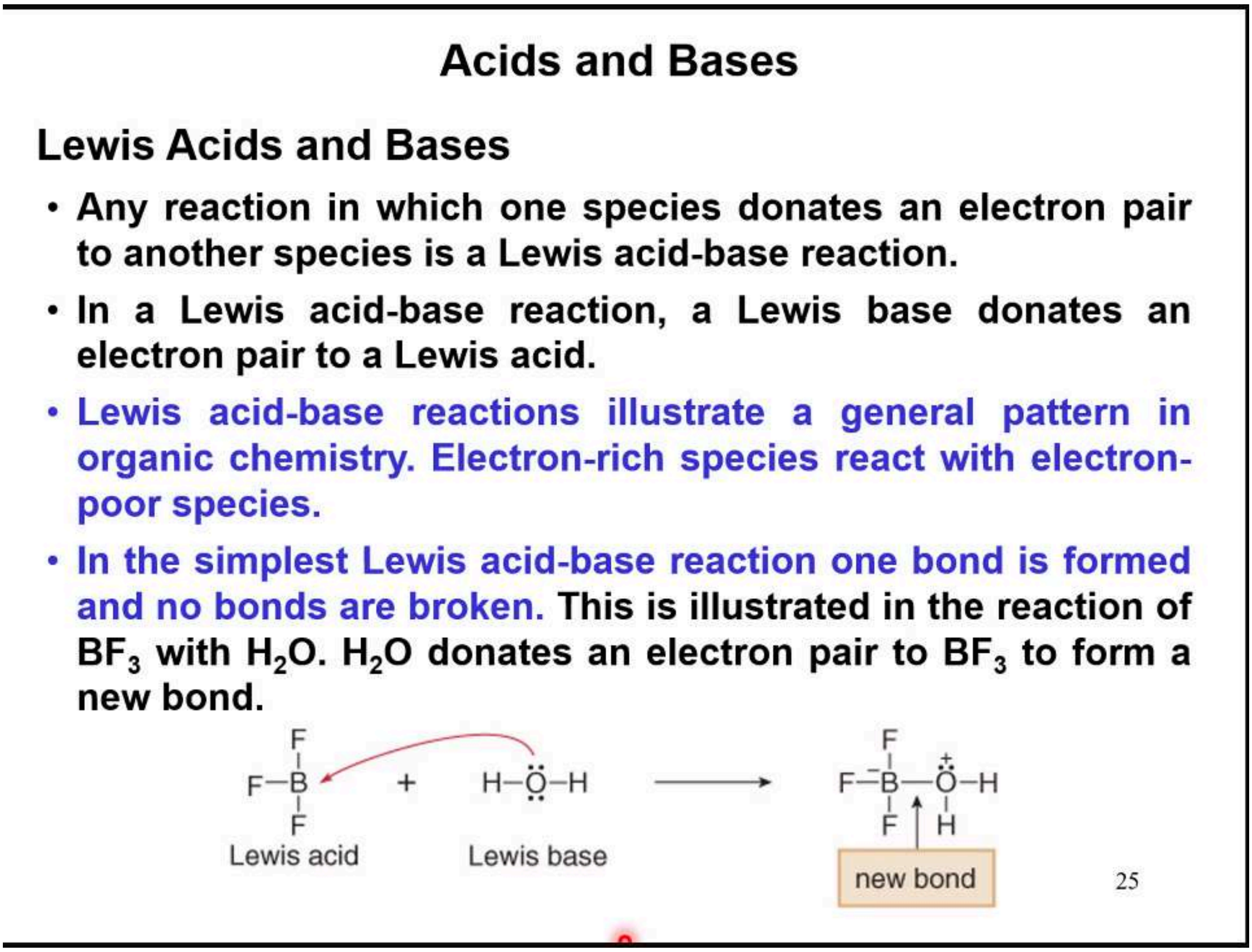
Lewis Acids and Bases

- All Brønsted-Lowry acids are also Lewis acids, but the reverse is not necessarily true.
  - o Any species that is electron deficient and capable of accepting an electron pair is also a Lewis acid.
- Common examples of Lewis acids (which are not Brønsted-Lowry acids) include BF_3 and $AlCl_3$. These compounds contain elements in group 3A of the periodic table that can accept an electron pair because they do not have filled valence shells of electrons.



Any reaction in which one species donates an electron pair to another species is a lewis acid-base reaction.
In a lewis acid-base reaction, a lewis base donates an electron pair to a lewis acid.

lewis acid-base reactions illustrate a general pattern in organic chemistry. electron rich species react with electron poor species



Acids and Bases

Lewis Acids and Bases

- **Any reaction in which one species donates an electron pair to another species is a Lewis acid-base reaction.**
- **In a Lewis acid-base reaction, a Lewis base donates an electron pair to a Lewis acid.**
- **Lewis acid-base reactions illustrate a general pattern in organic chemistry. Electron-rich species react with electron-poor species.**
- **In the simplest Lewis acid-base reaction one bond is formed and no bonds are broken. This is illustrated in the reaction of BF_3 with H_2O. H_2O donates an electron pair to BF_3 to form a new bond.**

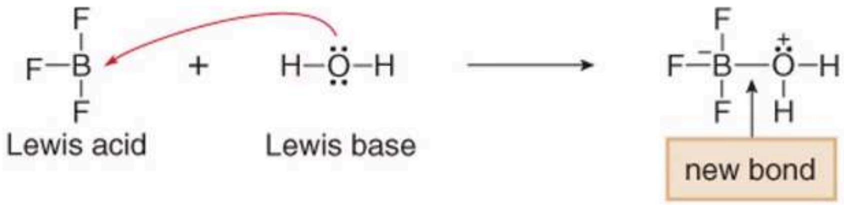
lewis acid is also a called an electrophile = e^+ = electronpoor

When a lewis base reacts with an electrophile other than a proton, the lewis base is also called a nucleophile = $Nu:^-$

Acids and Bases

Lewis Acids and Bases

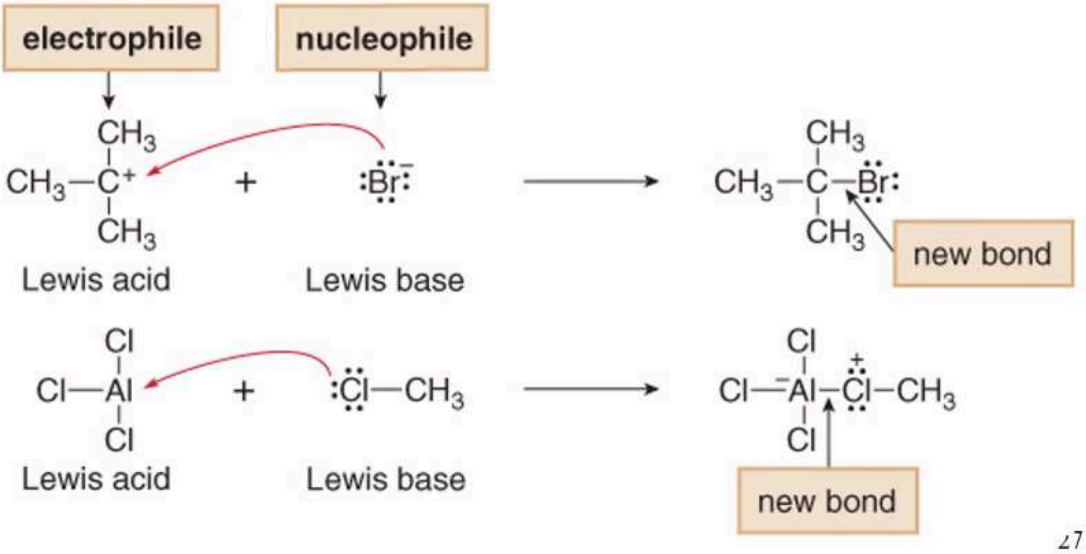
- **A Lewis acid is also called an electrophile.**
- **When a Lewis base reacts with an electrophile other than a proton, the Lewis base is also called a nucleophile. In this example, BF_3 is the electrophile and H_2O is the nucleophile.**



Acids and Bases

Lewis Acids and Bases

- **Note that in each reaction, the electron pair is donated to an atom of the Lewis acid and one new covalent bond is formed.**



Chapter 3: Introduction to Organic Molecules and Functional Groups

Organic molecules:
R (carbon skeleton) bonded to a functional group (Heteroatoms) or π bonds C=C and C=0

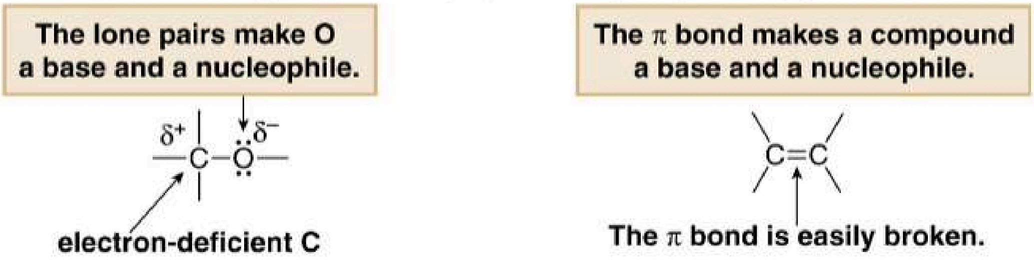
Functional group:
distinguish one organic molecule from another
determine a molecules

- geometry
- physical properties
- chemical reactivity

heteroatoms
electronegative N, O , Halogens
two lone electrons and create electro deficient sites on C.

Functional Groups: Heteroatoms and π bonds

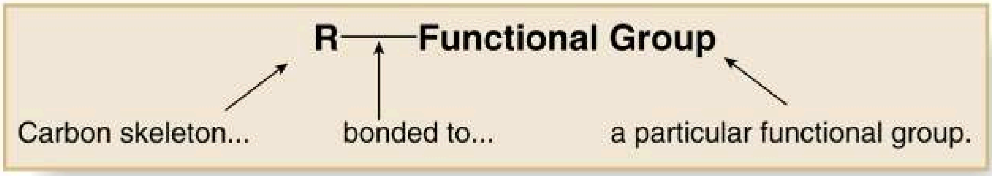
1. **Heteroatoms:**
   1) electronegative N, O, X
   2) have lone $2e^-$ and create e^--deficient sites on C.
2. **π bond: react as a base and a nucleophile**



The lone pairs make O a base and a nucleophile.

The π bond makes a compound a base and a nucleophile.

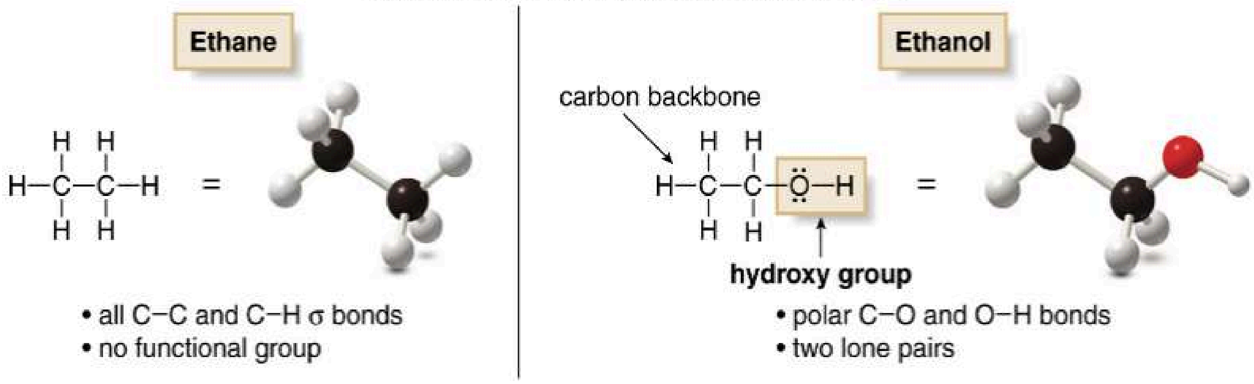
An Example of a Functional Group



R—Functional Group

Carbon skeleton... bonded to... a particular functional group.

Carbon skeleton



- all C–C and C–H σ bonds
- no functional group

- polar C–O and O–H bonds
- two lone pairs

ethane: no functional group, no polar bonds, lone pairs, or pi bonds - unreactive
ethanol: have a functional group, 2 lone pairs and polar bonds causes reactivity

classification of hydrocarbons
aliphatic or aromatic
alkane - single bond
alkene - double bond
alkyne- triple bond
aromatic compound - phenyl - C6H6

primary carbon - bonded to one carbon
secondary - bonded to two
tertiary - bonded to three
quaternary - bonded to four

primary hydrogen - carbon its bonded to bonded to one other carbon
secondary hydrogen- carbon its bonded to bonded to two other carbon
tertiary hydrogen - carbon its bonded to bonded to three other carbon.

functional group with carbon heteroatom
heteroatom creates a polar bond - electronegative gets electrons, makes heteroatom electron rich while carbon is electro deficient

electronegativity- atoms ability to attract electrons

alkyle halide R-Halogen (F, CL, BR, I)- HALO GROUP
ALCOHOL - R-OH hydroxy group
ether R-O-R alkoxy group
R-NH2 or R2-NH or R3N = amine amino group
Thiol = R-SH mercapto group
sulfide R-S-R alkylthio group

ETHER = SULFIDE BUT ETHER IS OXYGEN SULFIDE IS SULFUR
THEY HAVE TWO RS ON THEIR SIDE

OH AND SH is O AND S WITH HYDROGEN TO FULFILL THEIR NEED TO HAVE ANOTHER BOND.

alkyl halides primary secondary tertiary like hydrogen

amines- classified by number of Carbon bonds to the nitrogen. primary secondary tertiary.

All organic molecules contain a hydrocarbon skeleton.
And organic molecules can also contain a functional group which gives it unique properties/

Alkane follows the formula C_nH_{2n+2}
Since there are N-2 of C that have H2
and 2 of C that have H3
H would be 2N - 4 + 6 = 2N + 2

For Alkenes that have one double bond: C_nH_{2n}
Each carbon would have lose a bond with 1 hydrogen
So since there are two carbons in one bond, they will lose 2 hydrogen in total.

For Alkynes C_nH_{2n-2}
Follows the pattern for Alkenes

Heteroatom

The electronegative Z creates a polar bond -> reative.

Partially negative charge on heteroatom
Partially positive charge on Carbon.

Alkyl Halide, Alkane - loses hydrogen (turns into Alkyl group)
Halide (negative charged halogen, turns into halide)

Alcohol - OH hydroxy group

Ether - OR alkoxy group

Amine - NH2 amino group

Thiol - SH mercapto group

Sulfide -SR alkylthio group

Carbonyl group C=O

- functional groups with a double bond with oxygen
  electron deficient C: electrophile
  electron rich O: nucleophile

Aldehyde C=O

Ketone- replaced Aldehyde H with another R

Carboxylic acid - instead of H, its OH

check if theres double bond O, if yes its carboxylic else alcohol

Ester- double O with OH not ether

Amide- like Amine but Amide has double O

Acid Chloride- lIke Alkyl Chloride but has C=O
reason its called Acid Chloride is that is acid + chloride

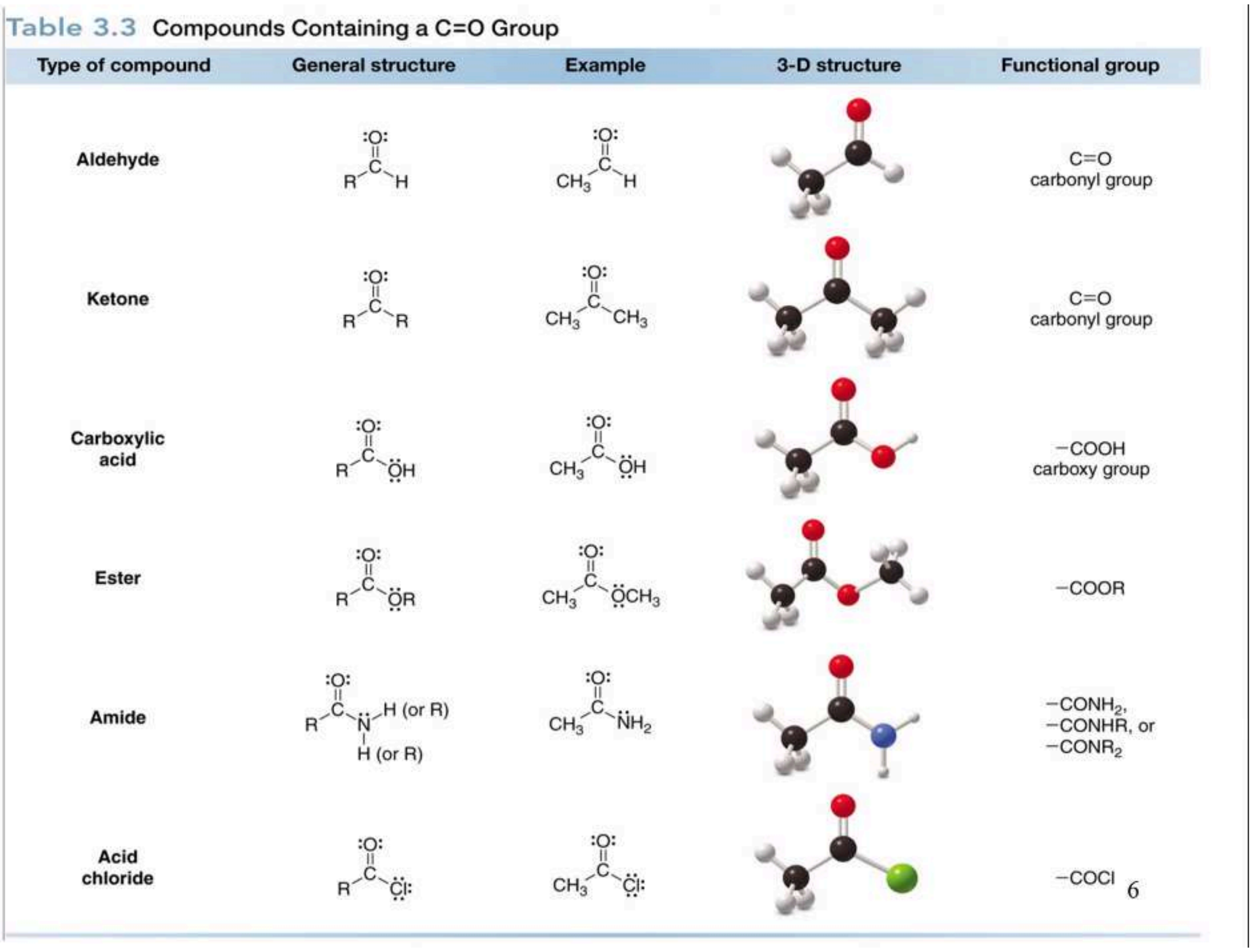
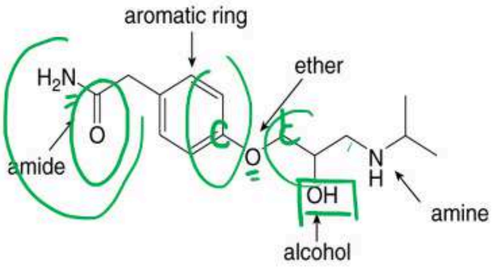


Table 3.3 Compounds Containing a C=O Group

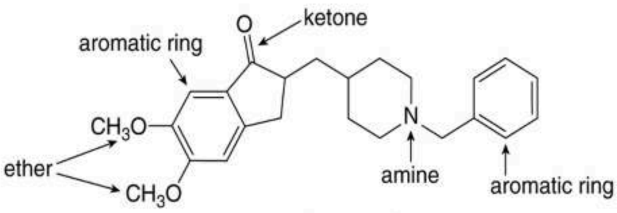
Type of compound	General structure	Example	3-D structure	Functional group
Aldehyde	$RCHO$	CH_3CHO		C=O carbonyl group
Ketone	$RCOR$	CH_3COCH_3		C=O carbonyl group
Carboxylic acid	$RCOOH$	CH_3COOH		−COOH carboxy group
Ester	$RCOOR$	CH_3COOCH_3		−COOR
Amide	$RCON$ H (or R) H (or R)	CH_3CONH_2		$-CONH_2$, −CONHR, or $-CONR_2$
Acid chloride	$RCOCl$	CH_3COCl		−COCl

Organic Molecules with Several Functional Groups

Organic Molecules with Several Functional Groups

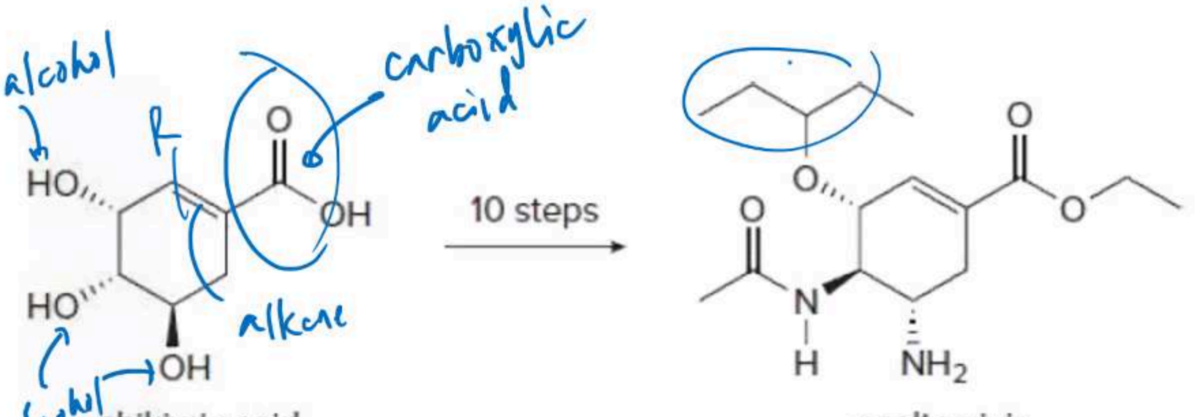


atenolol
(used to treat high blood pressure)



donepezil
(used to treat Alzheimer's disease)

Oseltamivir can be prepared in 10 steps from shikimic acid. Identify the functional groups in oseltamivir and shikimic acid.



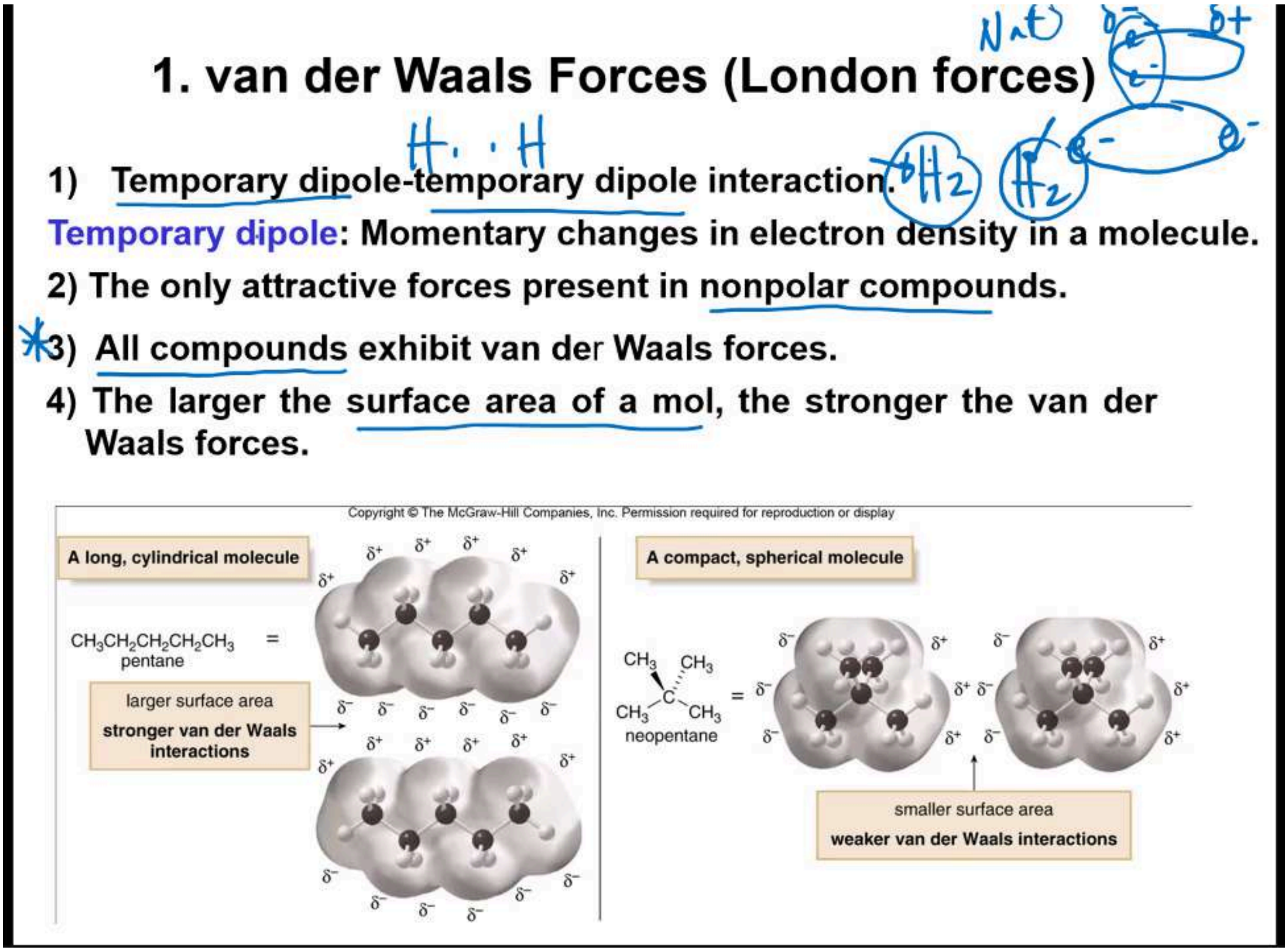
shikimic acid

oseltamivir

Importance of Functional Groups

1. Bonding and shape
2. Nomenclature
3. Physical Properties
4. Chemical reactivity
5. Type and strength of intermolecular forces

van der waals



1. van der Waals Forces (London forces)

1) Temporary dipole-temporary dipole interaction.

Temporary dipole: Momentary changes in electron density in a molecule.

2) The only attractive forces present in nonpolar compounds.

*3) All compounds exhibit van der Waals forces.

4) The larger the surface area of a mol, the stronger the van der Waals forces.

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A long, cylindrical molecule

$CH_3CH_2CH_2CH_2CH_3$ =
pentane

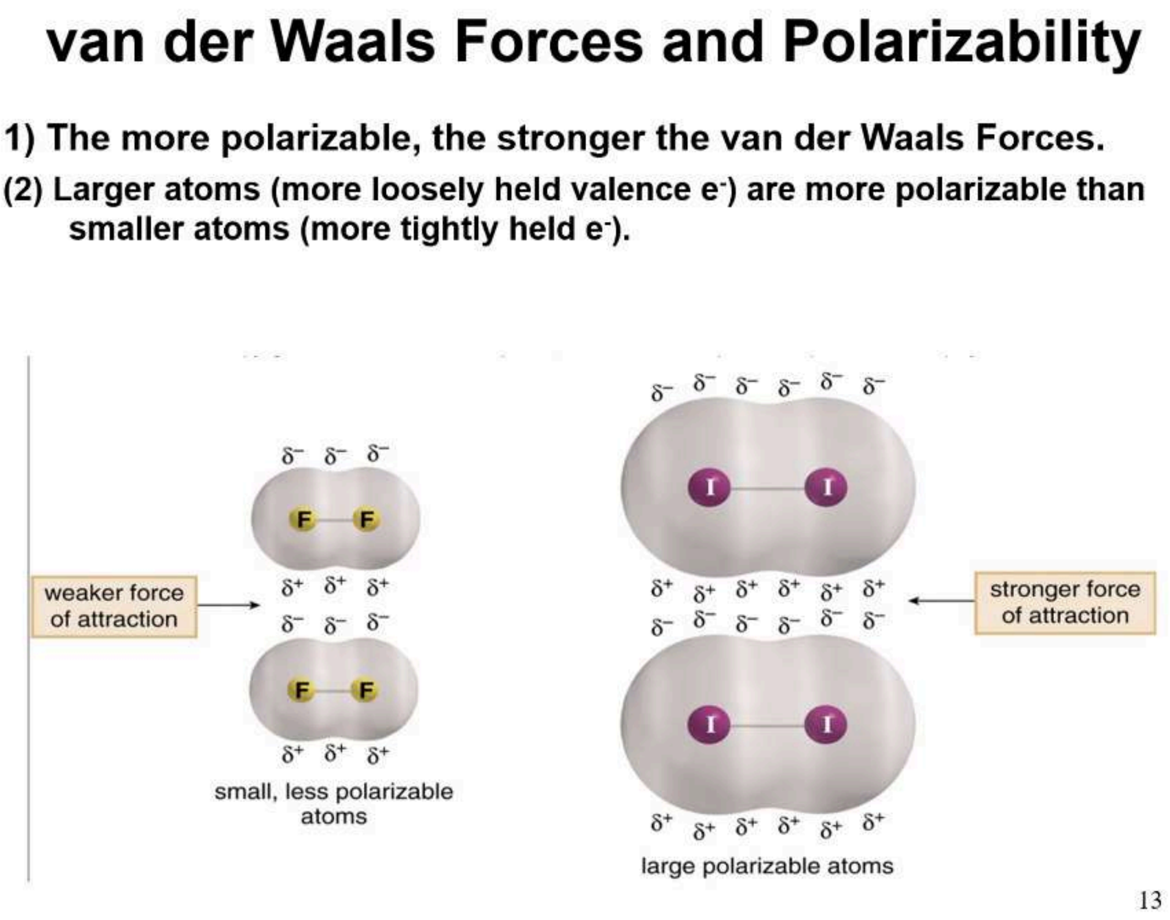
larger surface area
stronger van der Waals interactions

A compact, spherical molecule

neopentane =

smaller surface area
weaker van der Waals interactions

the more polarizable, the stronger the van der waals
larger atoms are more polarizable than smaller atoms



van der Waals Forces and Polarizability

1) The more polarizable, the stronger the van der Waals Forces.

(2) Larger atoms (more loosely held valence e^-) are more polarizable than smaller atoms (more tightly held e^-).

small, less polarizable atoms

large polarizable atoms

van der waals exist in all molecules but in non polar molecules they only exhibit van der waals

polar molecules exhibit dipole-dipole interactions

2. Dipole–Dipole Interactions

→ polar

polar

1) **Dipole-dipole interactions:** **the permanent dipole-dipole interactions between polar molecules.**

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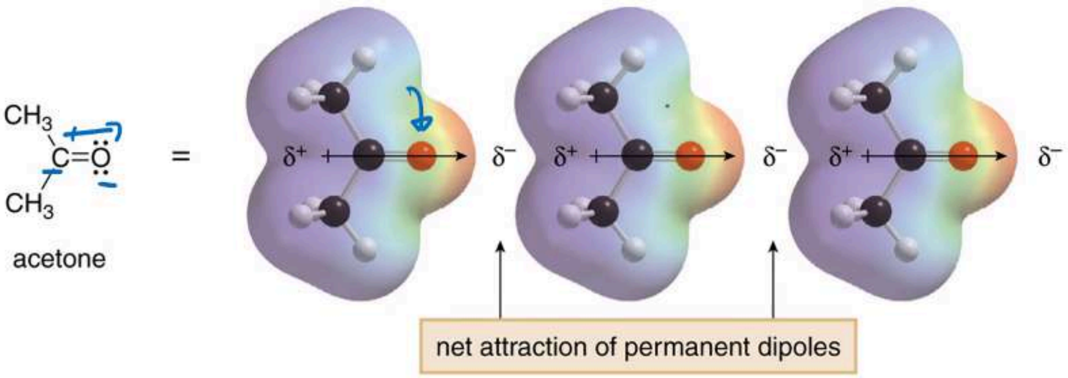

3. Hydrogen Bonding

1) **Very strong dipole-dipole interactions.**
2) **Between H (bonded to electronegative elements (O, N, X) and a lone pair ($2e^-$) on an electronegative element.**

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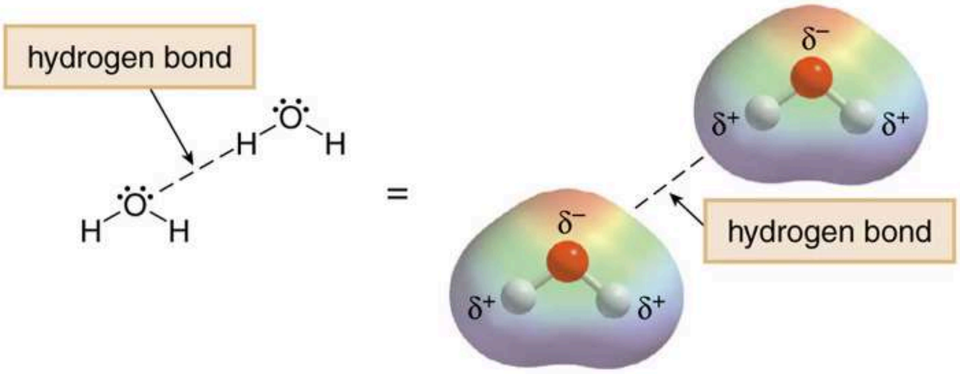
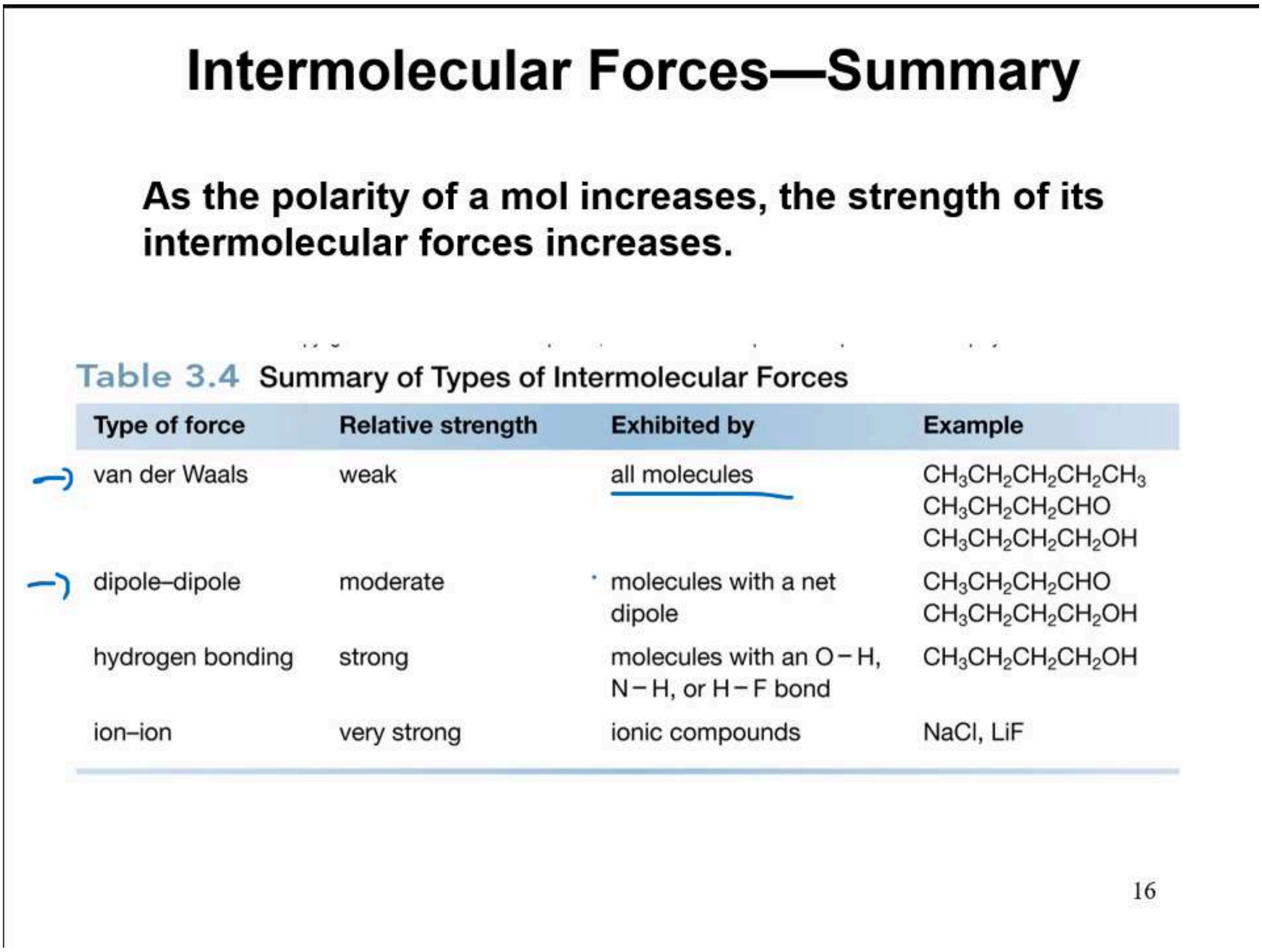


between H bonded to electro negative elements and another electronegative element



Intermolecular Forces—Summary

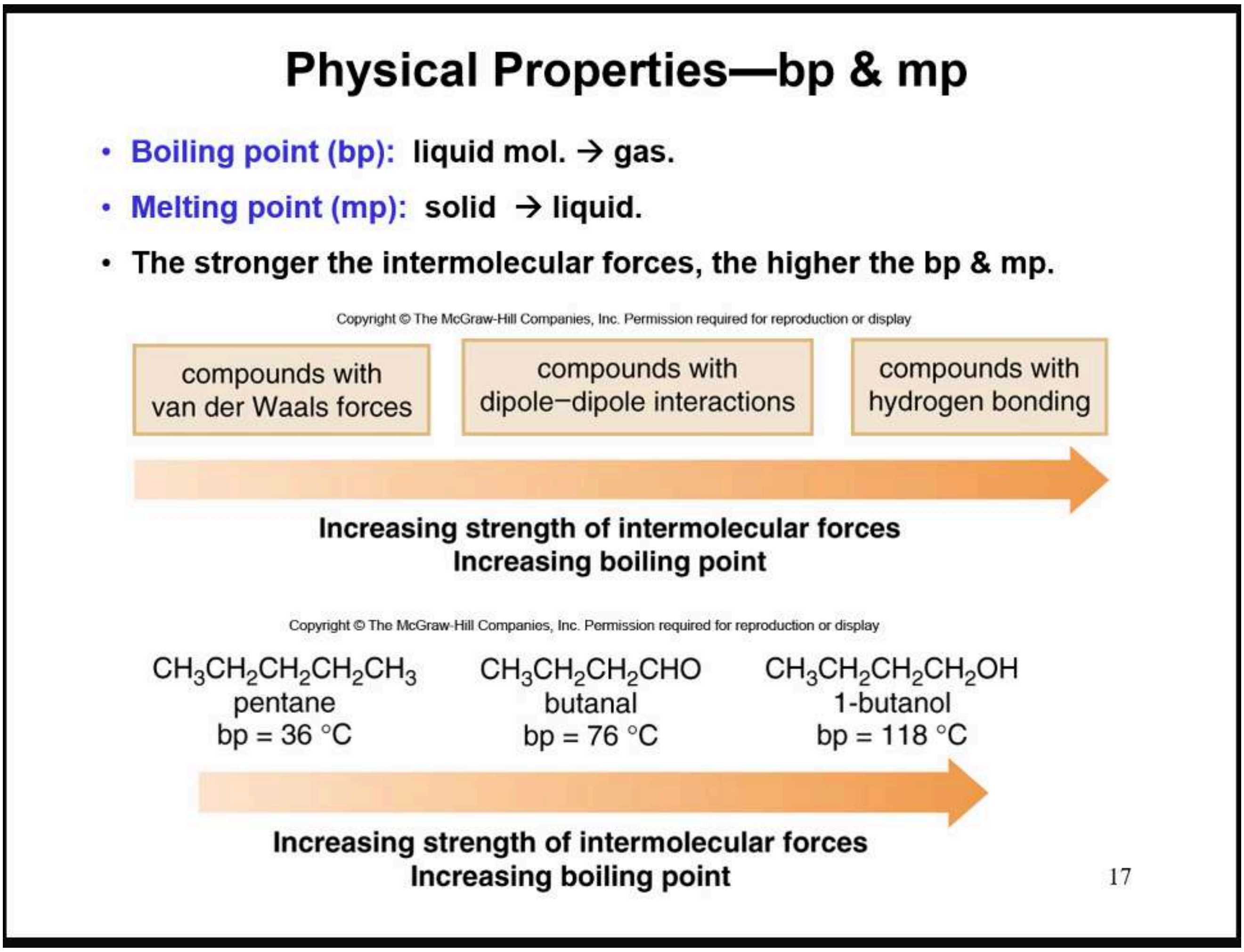
As the polarity of a mol increases, the strength of its intermolecular forces increases.

Table 3.4 Summary of Types of Intermolecular Forces

Type of force	Relative strength	Exhibited by	Example
van der Waals	weak	all molecules	$CH_3CH_2CH_2CH_2CH_3$ $CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
dipole–dipole	moderate	molecules with a net dipole	$CH_3CH_2CH_2CHO$ $CH_3CH_2CH_2CH_2OH$
hydrogen bonding	strong	molecules with an O−H, N−H, or H−F bond	$CH_3CH_2CH_2CH_2OH$
ion–ion	very strong	ionic compounds	NaCl, LiF

alcohol -hydrogen bonding

ion-ion mostly inorganic molecules
dipole-dipole needs lewis bonds



Physical Properties—bp & mp

- **Boiling point (bp):** liquid mol. → gas.
- **Melting point (mp):** solid → liquid.
- **The stronger the intermolecular forces, the higher the bp & mp.**

compounds with van der Waals forces

compounds with dipole−dipole interactions

compounds with hydrogen bonding

Increasing strength of intermolecular forces
Increasing boiling point

$CH_3CH_2CH_2CH_2CH_3$
pentane
bp = 36 °C

$CH_3CH_2CH_2CHO$
butanal
bp = 76 °C

$CH_3CH_2CH_2CH_2OH$
1-butanol
bp = 118 °C

Increasing strength of intermolecular forces
Increasing boiling point

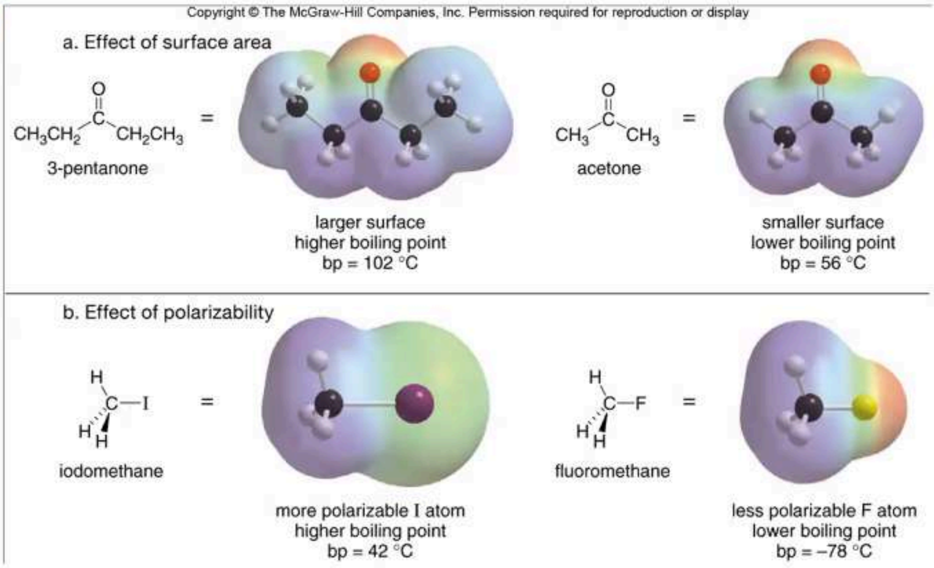
strongest bonds - highest boiling points and melting points

in examination, no specific boiling points but arrangement of organic molecules according to increasing decreasing boiling point

Other Factors Affecting Boiling Points

- For compounds with similar functional groups:
  - The larger the surface area, the higher the bp.
  - The more polarizable the atoms, the higher the bp.

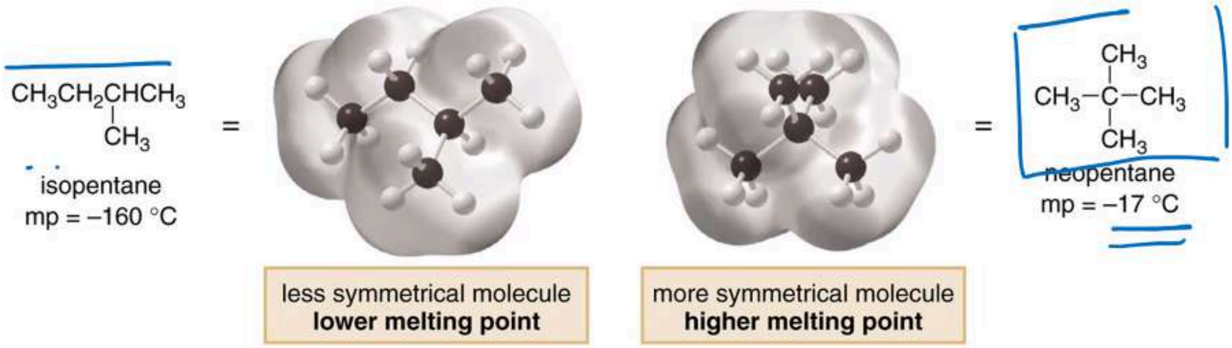
Figure 3.2

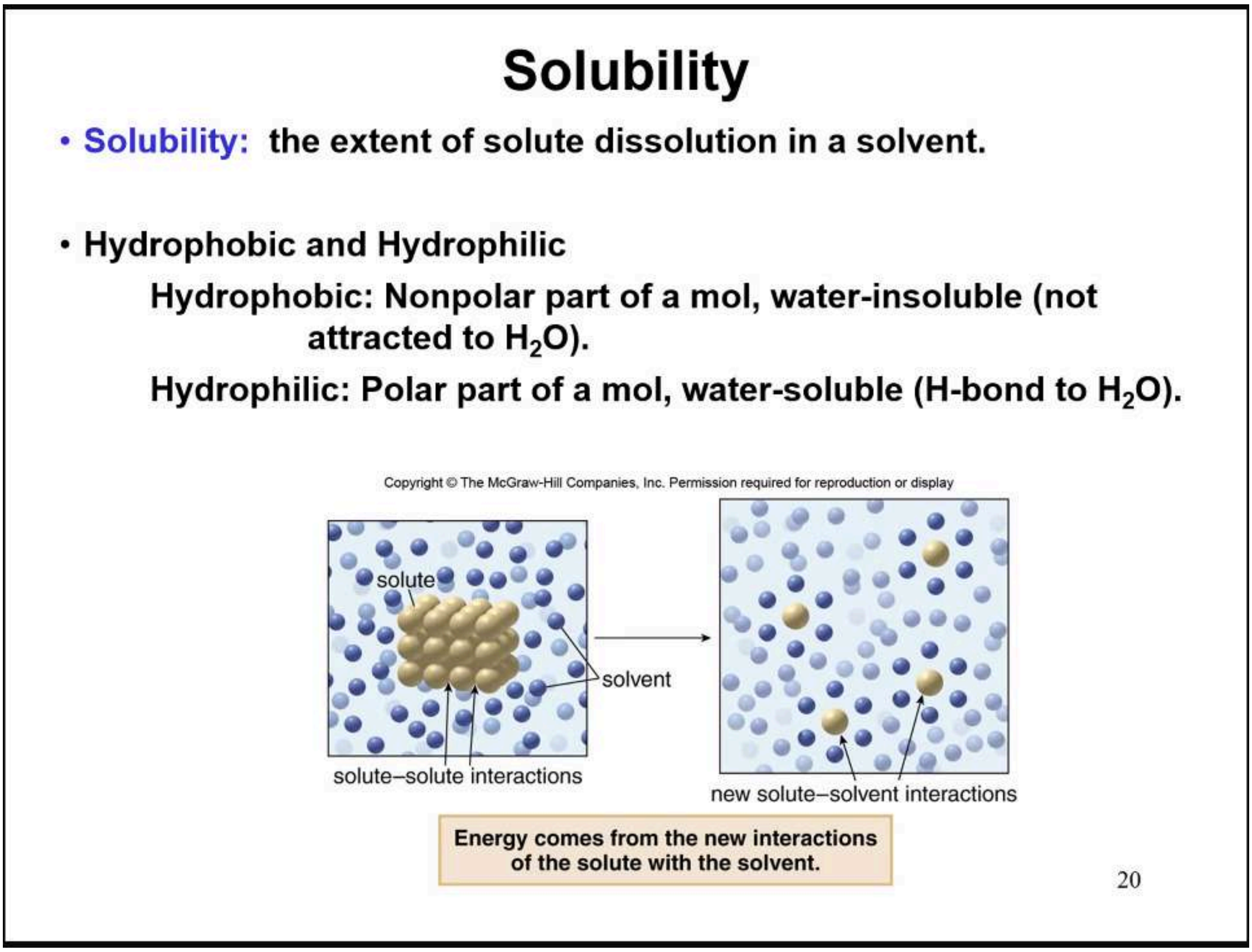


Effect of Symmetry on Melting Points

- The more compact and symmetrical the shape (a crystalline lactice), the higher the mp.

Ex) Neopentane has a much higher mp than isopentane.





Solubility

- **Solubility:** the extent of solute dissolution in a solvent.
- **Hydrophobic and Hydrophilic**
  - Hydrophobic: Nonpolar part of a mol, water-insoluble (not attracted to H_2O).
  - Hydrophilic: Polar part of a mol, water-soluble (H-bond to H_2O).

Energy comes from the new interactions of the solute with the solvent.

like dissolves like

ionic and polar dissolve in polar

non polar and weakly polar dissovles in non polar and weakly polar

solubility of organic molecules
realtive size of nonpolar to polar porition
water soluble < 5C for one functional group

Nomenclature

The name of every organic molecule has 3 parts:

1. The parent name indicates the number of carbons in the longest continuous chain.
2. The suffix indicates what functional group is present
3. The prefix tells us the identity, location and number of substituents attached to the carbon chain.
   1. Prefix - what and where are the substituents?
   2. Parent- what is the longest carbon chain?
   3. Suffix- what is the functional group?

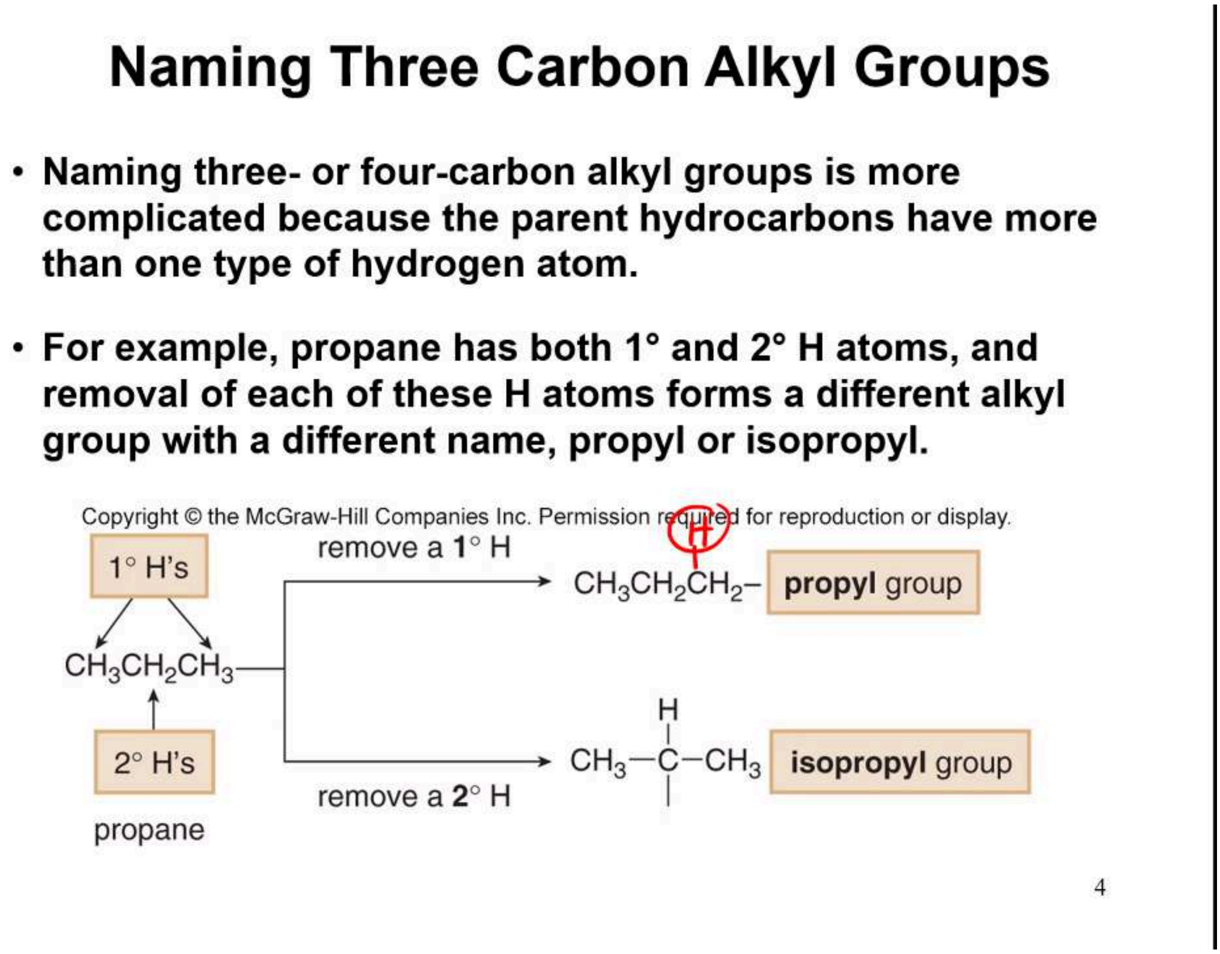
Naming Substituents

Alkyl Groups

- Carbon substituents a bonded to a long carbon chain are called alkyl groups
  - We remove one hydrogen so that we can attach this alkyl to the main carbon chain.
    - CH4 methane -> CH3 methyl
- To name an alkyl group, change the -ane ending of the parent alkane to -yl
- Thus methane becomes methyl and ethane becomes ethyl

Naming Three Carbon Alkyl Groups

- Naming three or four carbon alkyl groups is more complicated because the parent hydrocarbons have more than one type of hydrogen atom.
- Propane has both 1 and 2 H atoms, and the removal of each of these H atoms forms a different alkyl group with a different name, propyl or isopropyl
  - Terminal removed- primary H removed - propyl
  - Middle removed- secondary H removed - isopropyl



Naming Three Carbon Alkyl Groups

- **Naming three- or four-carbon alkyl groups is more complicated because the parent hydrocarbons have more than one type of hydrogen atom.**
- **For example, propane has both 1° and 2° H atoms, and removal of each of these H atoms forms a different alkyl group with a different name, propyl or isopropyl.**

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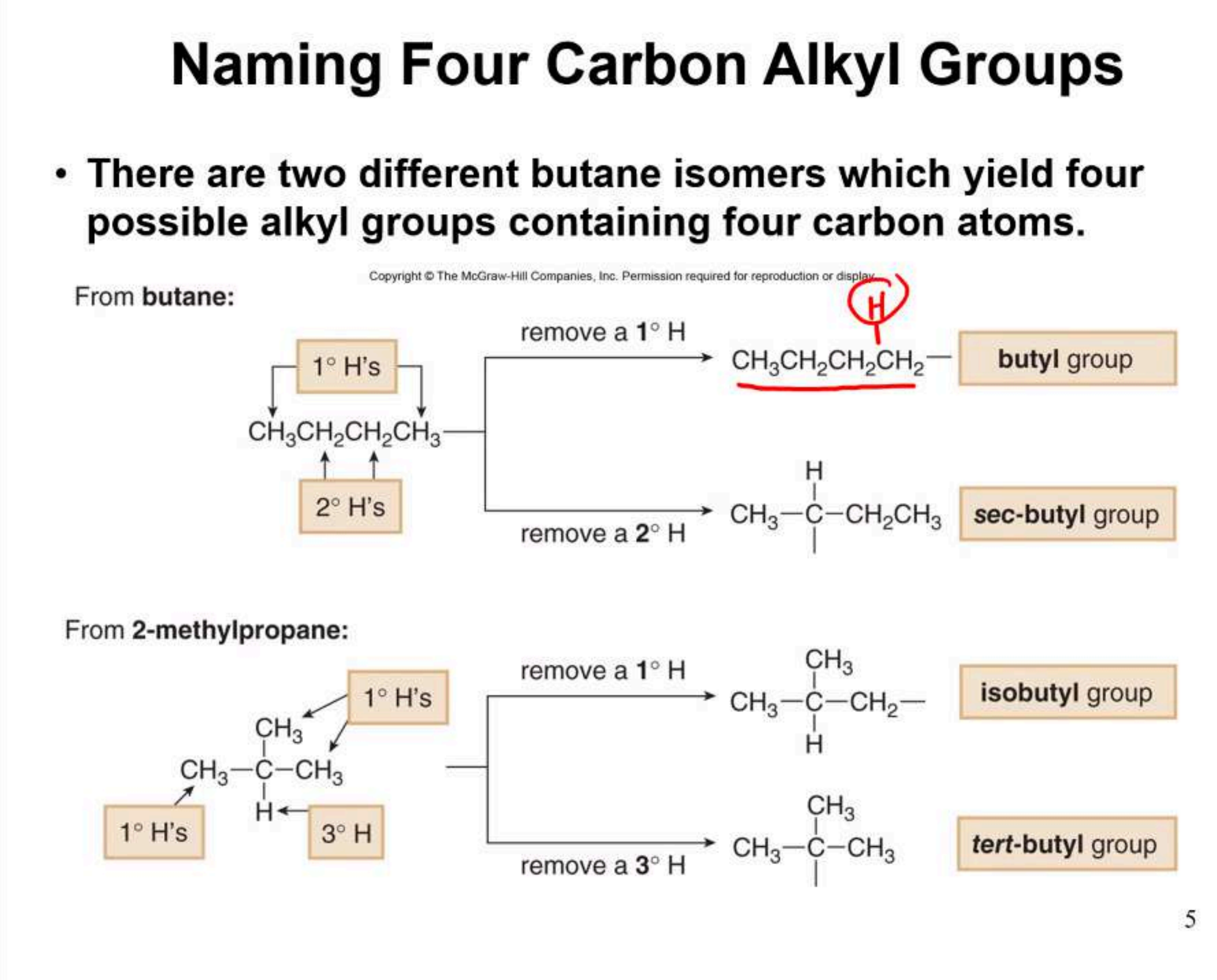
Naming Four Carbon Alkyl Groups

The prefix means what type of hydrogen you removed,
iso - 1 H
sec - 2 H
tert - 3 H

butyl - take one of the end.



Naming Four Carbon Alkyl Groups

- **There are two different butane isomers which yield four possible alkyl groups containing four carbon atoms.**

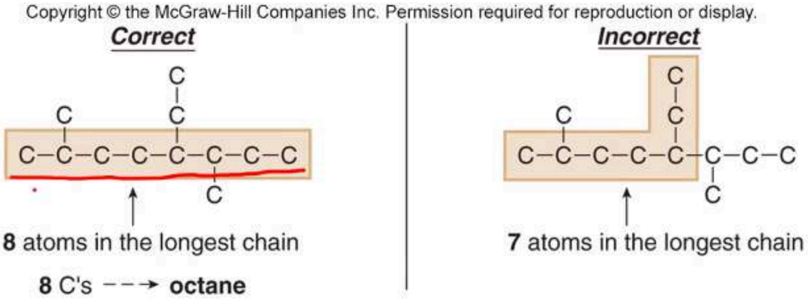
HOW TO NAME AN ALKANE USING THE IUPAC SYSTEM

1. FIND THE PARENT CARBON CHAIN AND ADD THE SUFFIX
    1. LONGEST CONTINOUS CHAIN - PARENT
        1. IT DOESNT HAVE TO BE LINEAR
2. Number the atoms in the carbon chain to give the first substituent the lowest number.
    1. If the first substituent is the same distance from both ends, number the chain to give the second substituent the lower number.
    2. When numbering a carbon chain results in the same numbers from either end of the chai, assign the lower number alphabetically to the first substituent
3. Name and number the substituents
    1. Name the substituents as alkyl groups
    2. Every carbon belongs to either the longest chain or substituent, not both
    3. Each substituent needs its own number
    4. If two or more identical substituents are bonded to the longest chain, use prefixes to indicate how many:
        1. di- 2
        2. tri- 3

        3. tetra- 4
        4. penta- 5
4. Combine substituent names and numbers + parent + suffix
    1. Precede the name of the parent by the name of substituents
    2. Alphabetize the names of the substituents ignoring all prefixes except iso, as in isopropyl and isobutyl
    1. Ignore sec or tert
    3. Precede the name of each substituent by the number that indicates its location
    4. Combine substituent names and numbers + parent + suffix
    5. Separate number by commas and separate numbers from letters by hyphens
    6. the name of an alkane is a single word, with no spaces after hyphens and commas

HOW TO Name an Alkane Using the IUPAC System

Step [1] Find the parent (longest continuous) carbon chain and add the suffix.



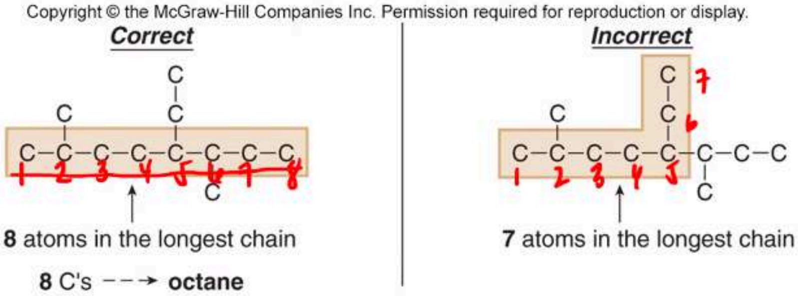
8 atoms in the longest chain

8 C's ⟶ **octane**

7 atoms in the longest chain

HOW TO Name an Alkane Using the IUPAC System

Step [1] Find the parent (longest continuous) carbon chain and add the suffix.

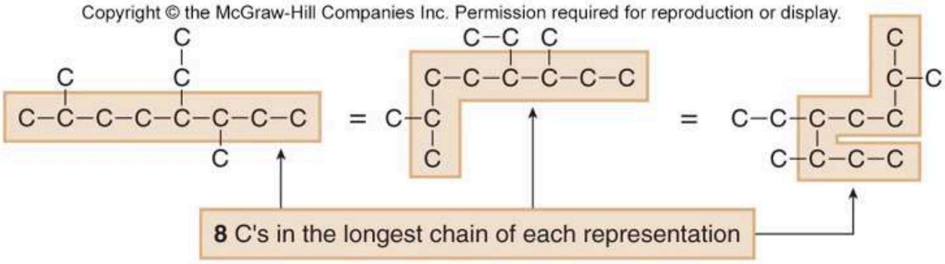


8 atoms in the longest chain

8 C's ⟶ **octane**

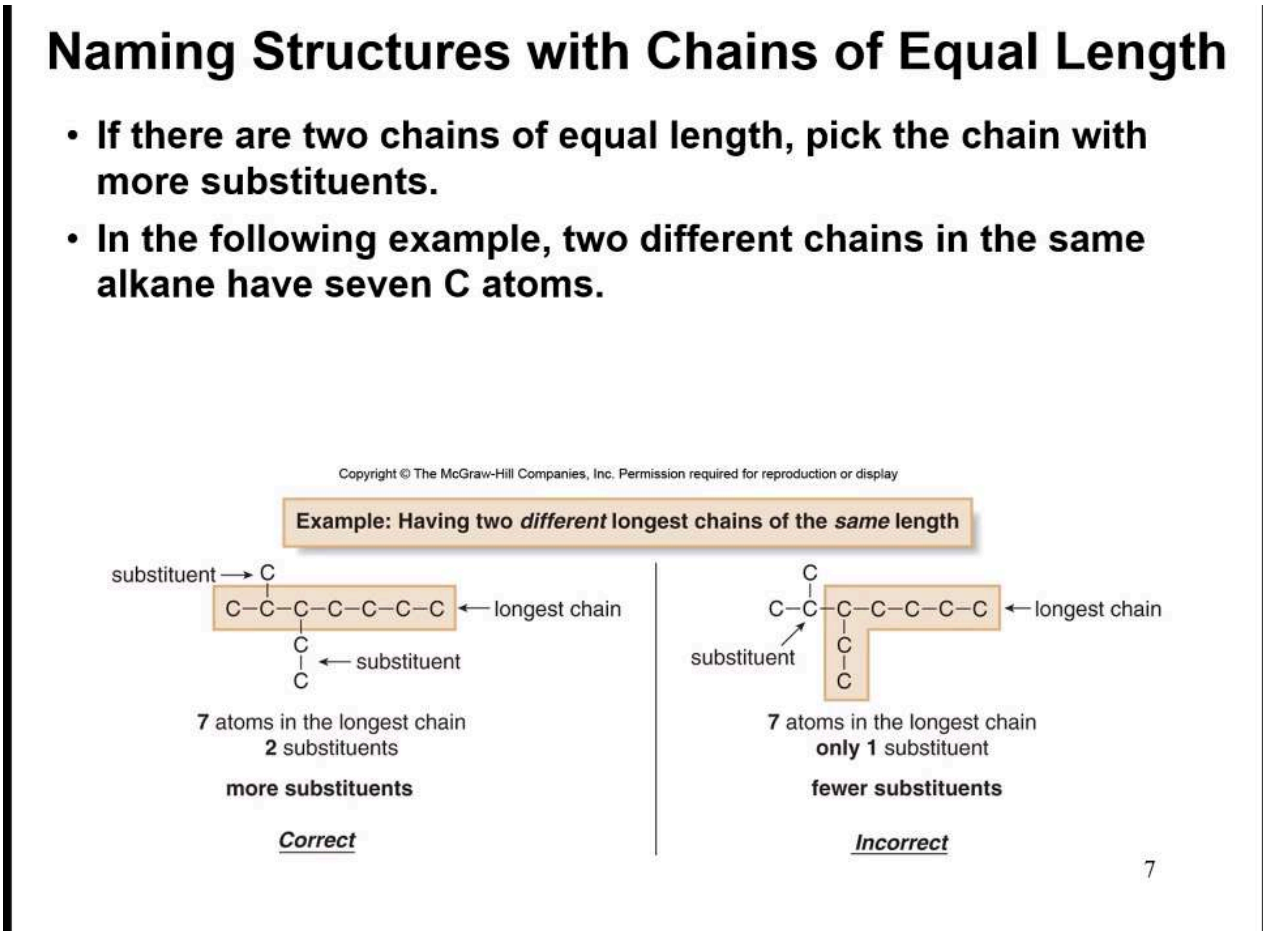
7 atoms in the longest chain

- **It does not matter if the chain is straight or it bends.**



8 C's in the longest chain of each representation

- If there a two chains of equal length pick the chain with more substituents



Naming Structures with Chains of Equal Length

- **If there are two chains of equal length, pick the chain with more substituents.**
- **In the following example, two different chains in the same alkane have seven C atoms.**

Example: Having two *different* longest chains of the *same* length

7 atoms in the longest chain
2 substituents

more substituents

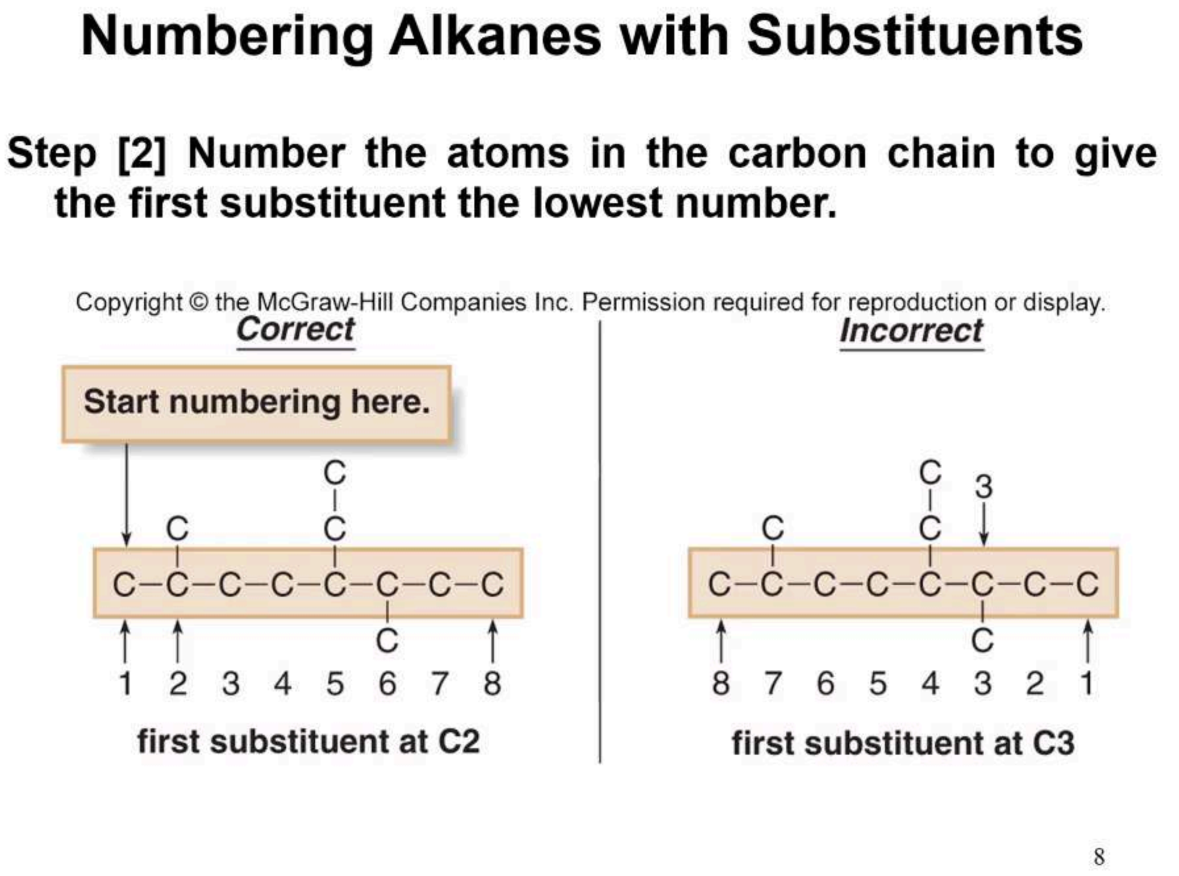
Correct

7 atoms in the longest chain
only 1 substituent

fewer substituents

Incorrect

Carbon can only be part of substituent or parent chain not both



Numbering Alkanes with Substituents

Step [2] Number the atoms in the carbon chain to give the first substituent the lowest number.

Correct

Start numbering here.

first substituent at C2

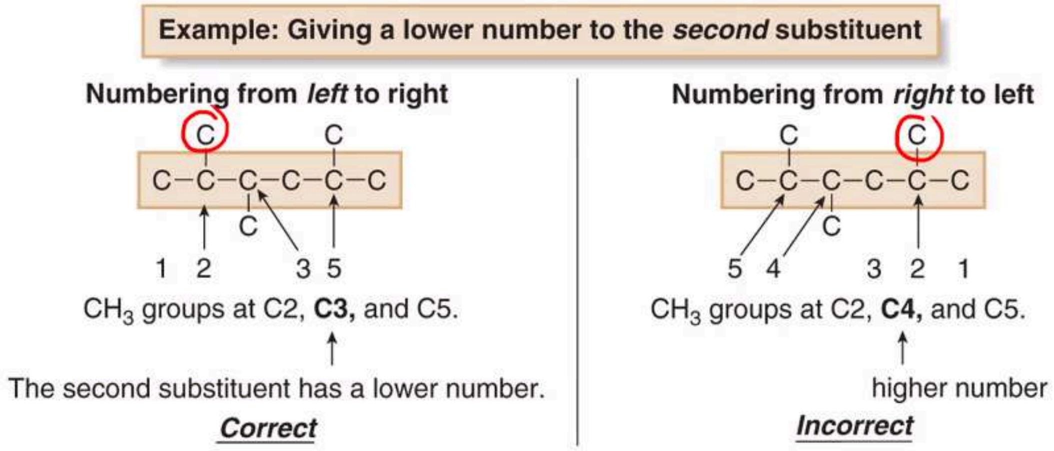
Incorrect

first substituent at C3

If there is one in both ends it depends on the type of substituent.

Numbering Substituents

If the first substituent is the same distance from both ends, number the chain to give the second substituent the lower number.



Example: Giving a lower number to the *second* substituent

Numbering from *left* to right

CH_3 groups at C2, **C3,** and C5.

The second substituent has a lower number.

Correct

Numbering from *right* to left

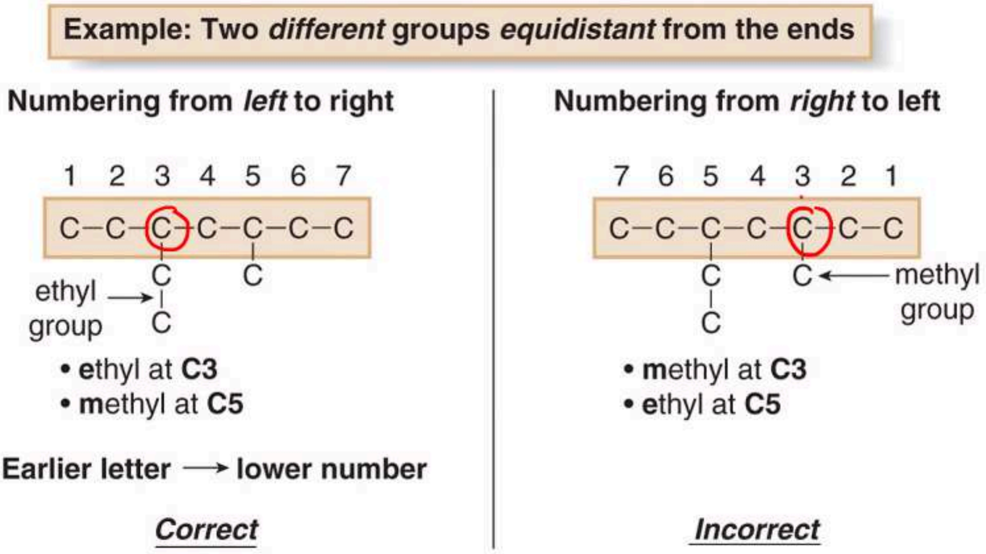
CH_3 groups at C2, **C4,** and C5.

higher number

Incorrect

Numbering Substituents

When numbering a carbon chain results in the same numbers from either end of the chain, assign the lower number alphabetically to the first substituent.



Example: Two *different* groups *equidistant* from the ends

Numbering from *left* to right

- **e**thyl at **C3**
- **m**ethyl at **C5**

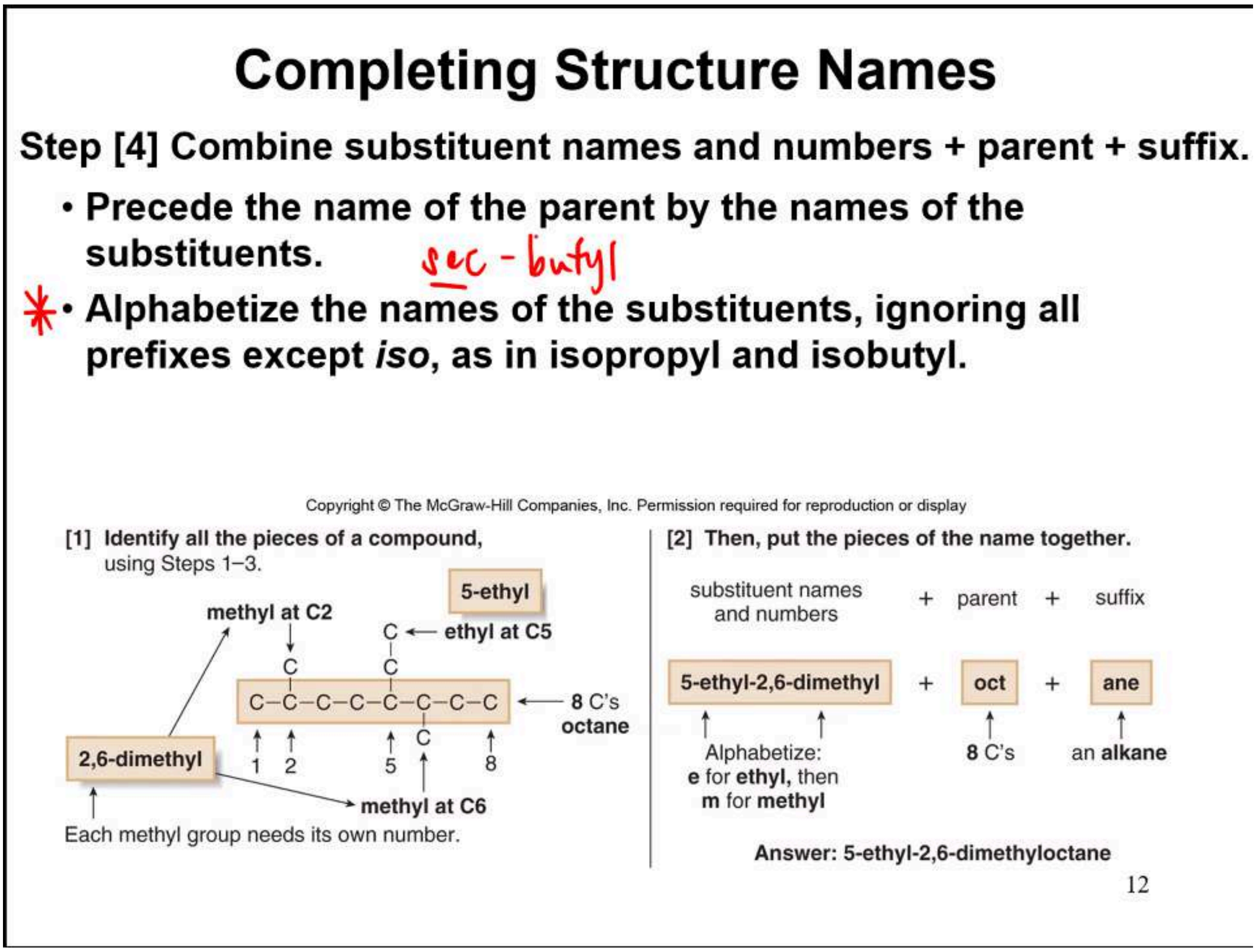
Earlier letter → lower number

Correct

Numbering from *right* to left

- **m**ethyl at **C3**
- **e**thyl at **C5**

Incorrect



Completing Structure Names

Step [4] Combine substituent names and numbers + parent + suffix.

- **Precede the name of the parent by the names of the substituents.** sec - butyl
- **Alphabetize the names of the substituents, ignoring all prefixes except *iso*, as in isopropyl and isobutyl.**

[1] Identify all the pieces of a compound, using Steps 1–3.

Each methyl group needs its own number.

[2] Then, put the pieces of the name together.

substituent names and numbers	+	parent	+	suffix
5-ethyl-2,6-dimethyl	+	**oct**	+	**ane**
Alphabetize: **e** for **ethyl**, then **m** for **methyl**		**8** C's		an **alkane**

Answer: 5-ethyl-2,6-dimethyloctane

5-ethyl-2,6-dimethyloctane

dash between 5-e and l-2

comma to separate numbers

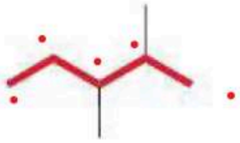
6-d

comma between numbers

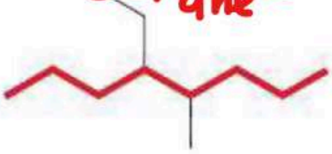
dashes between numbers and letters

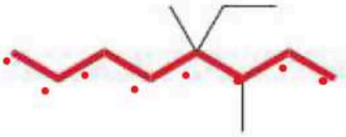
Give the IUPAC name of the following.

2,3-dimethylpentane

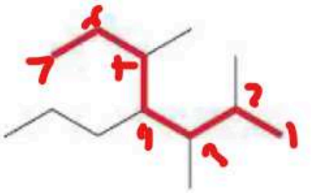


4-ethyl-dimethyl octane



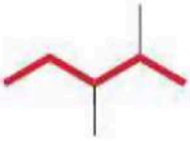


4 butyl- 3-methyl octane

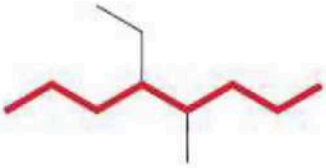


4-ethyl-2,3,5-trimethyl heptane

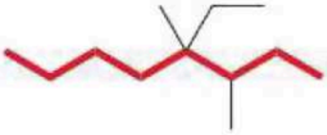
Give the IUPAC name of the following.



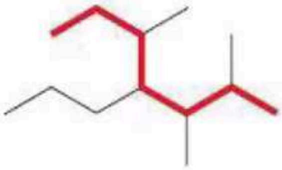
2,3-dimethylpentane



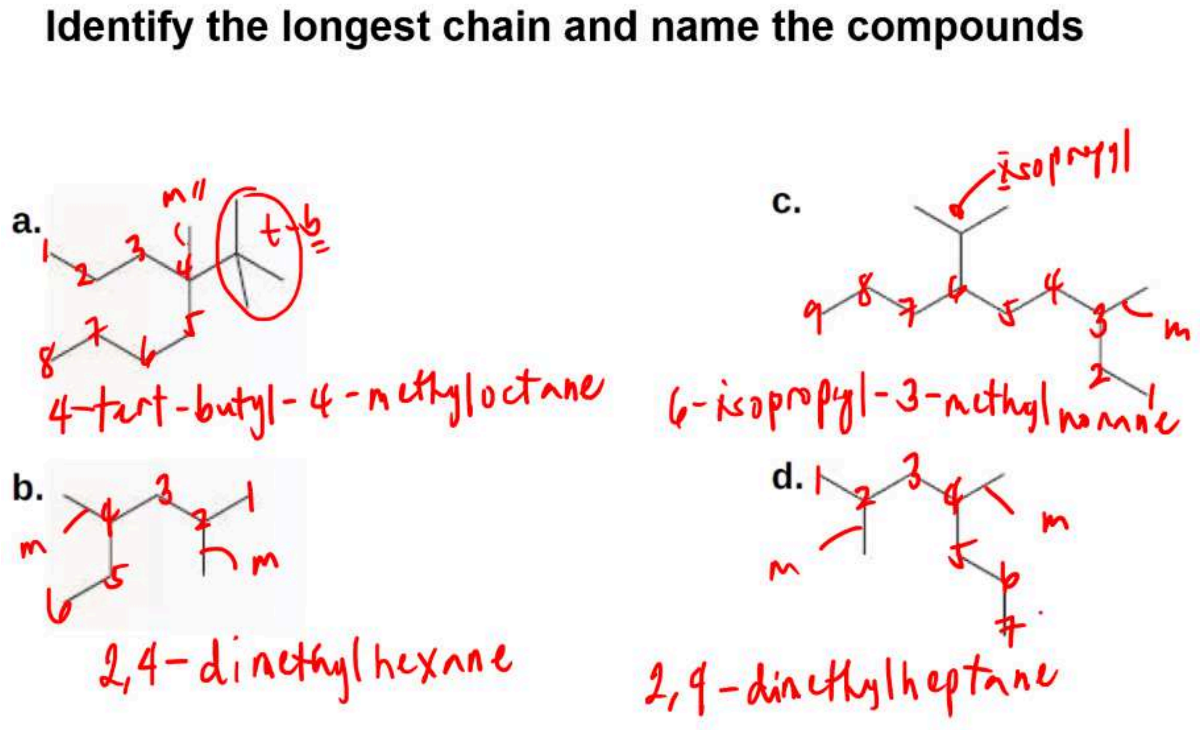
4-ethyl-5-methyloctane



4-ethyl-3,4-dimethyloctane



2,3,5-trimethyl-4-propylheptane



Identify the longest chain and name the compounds

a. 4-tert-butyl-4-methyloctane

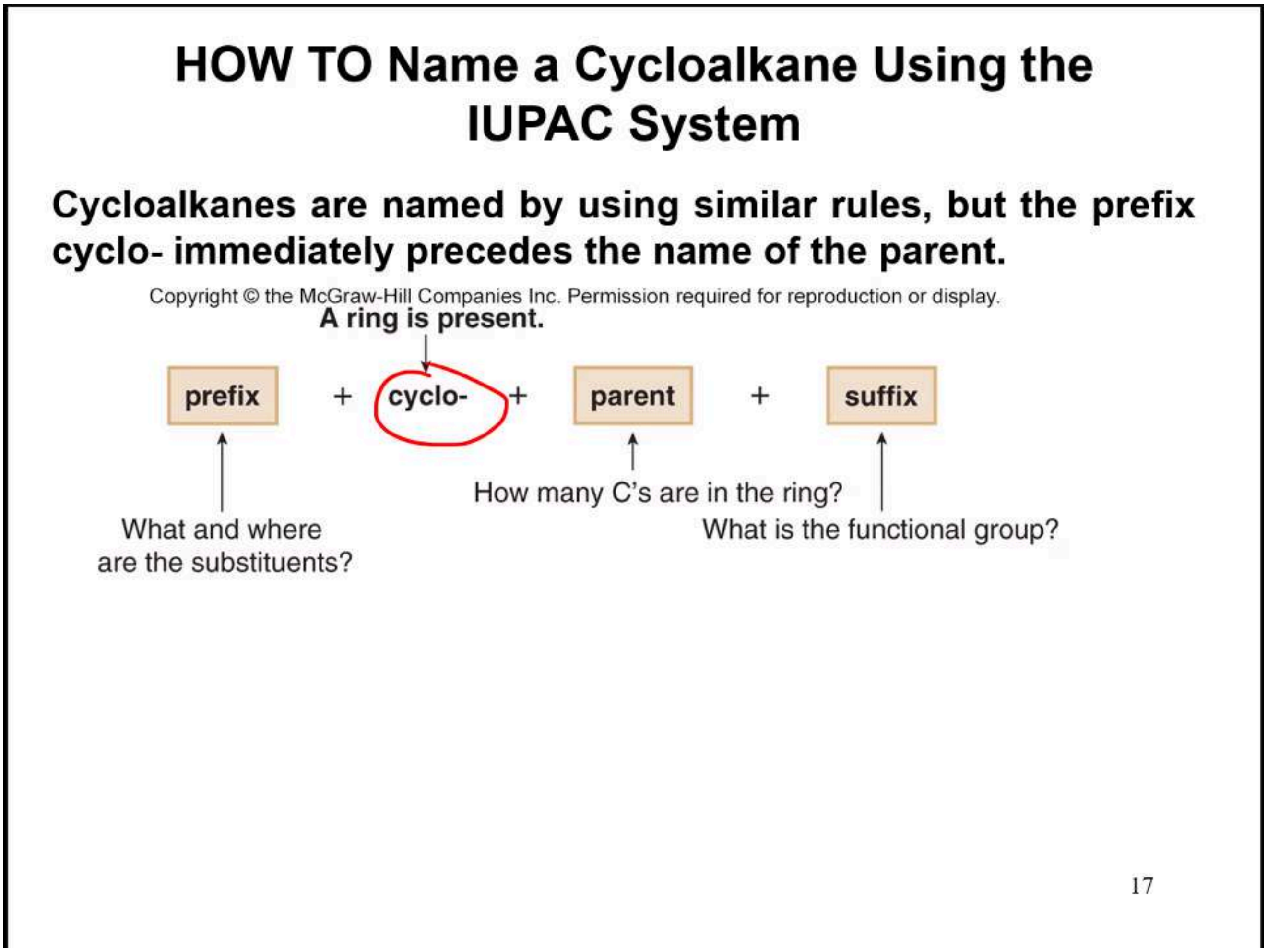
c. 6-isopropyl-3-methylnonane

b. 2,4-dimethylhexane

d. 2,4-dimethylheptane

HOW TO NAME A CYCLOALKNE USING THE IUPAC SYSTEM

Cycloalkanes are named by using similar rules, but the prefix cyclo immediately precedes the name of the parent.



HOW TO Name a Cycloalkane Using the IUPAC System

Cycloalkanes are named by using similar rules, but the prefix cyclo- immediately precedes the name of the parent.

A ring is present.

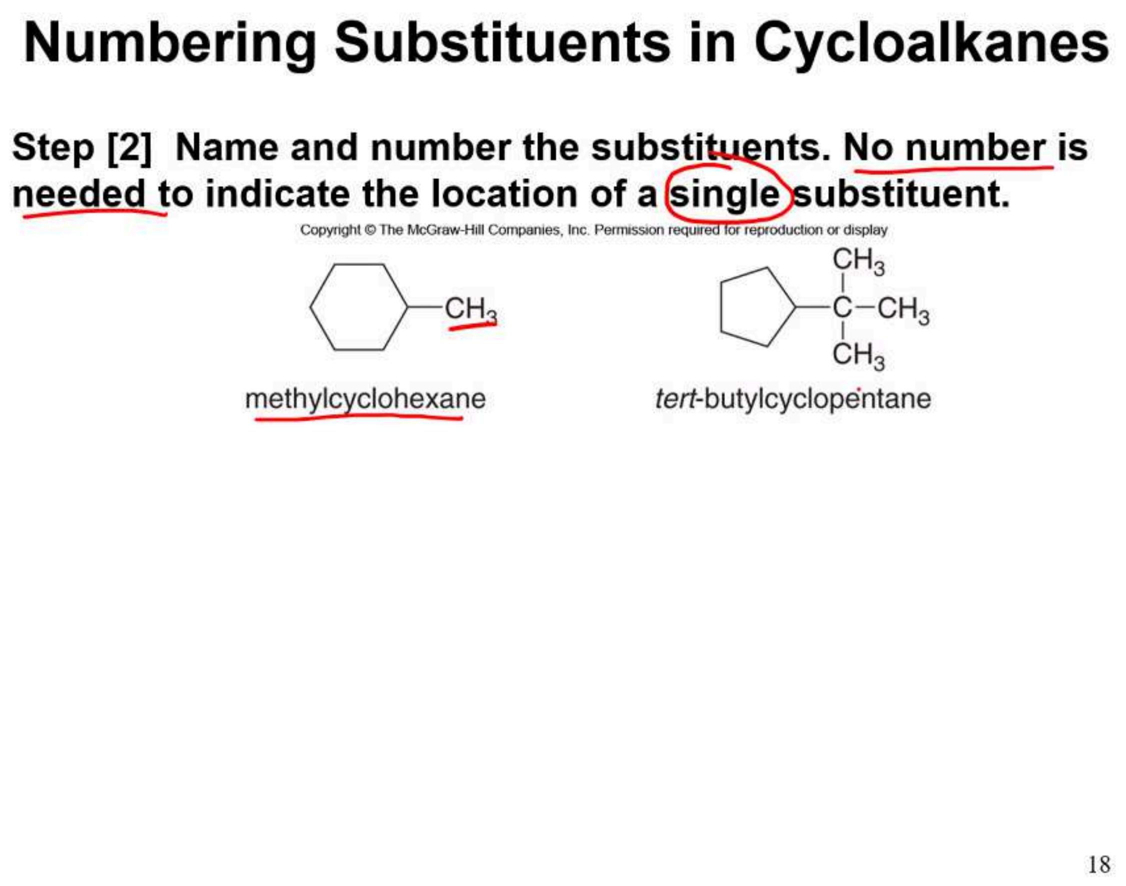
prefix + **cyclo-** + **parent** + **suffix**

What and where are the substituents?

How many C's are in the ring?

What is the functional group?

1. Find the parent cycloalkane
2. Name and the number the substituents. No number is needed to indicate the location of a single substituent



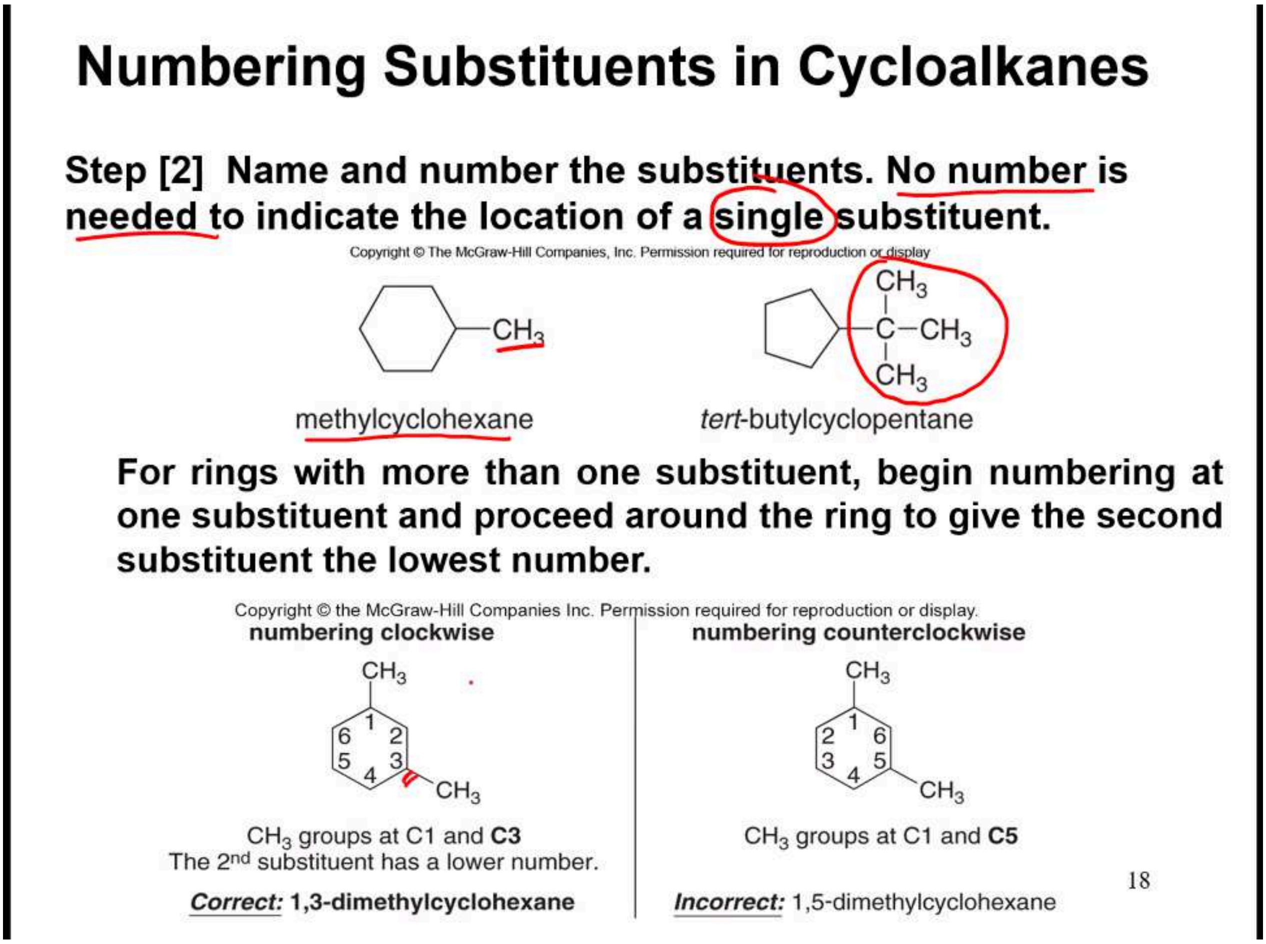
Numbering Substituents in Cycloalkanes

Step [2] Name and number the substituents. No number is needed to indicate the location of a single substituent.

methylcyclohexane

tert-butylcyclopentane

For rings with more than one subtituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.



Numbering Substituents in Cycloalkanes

Step [2] Name and number the substituents. No number is needed to indicate the location of a single substituent.

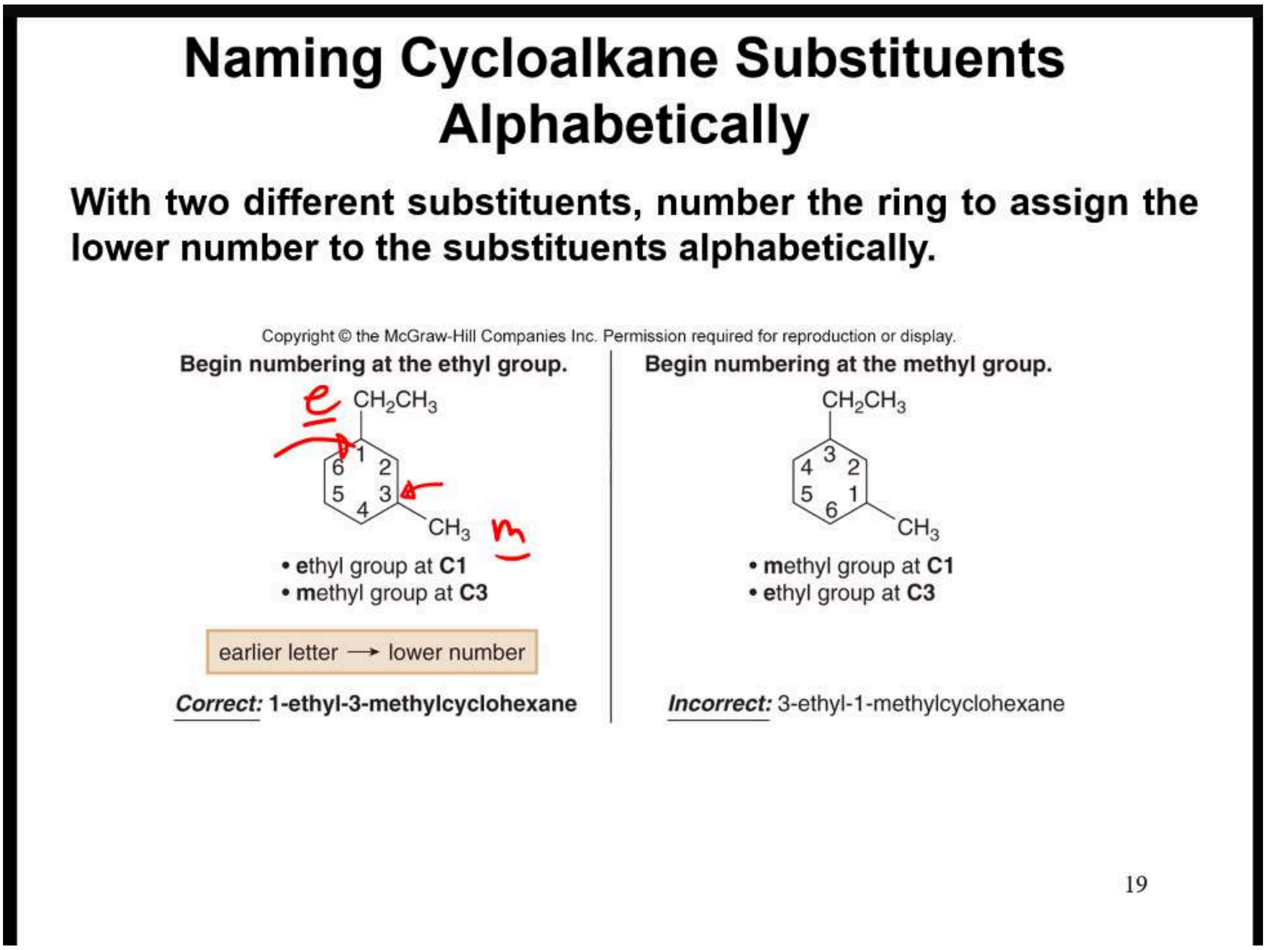
methylcyclohexane

tert-butylcyclopentane

For rings with more than one substituent, begin numbering at one substituent and proceed around the ring to give the second substituent the lowest number.

numbering clockwise	**numbering counterclockwise**
CH$_3$ groups at C1 and **C3** The 2nd substituent has a lower number.	CH$_3$ groups at C1 and **C5**
Correct: **1,3-dimethylcyclohexane**	***Incorrect:*** 1,5-dimethylcyclohexane

With two different substituents, number the ring to assign the lower number to the substituents alphabetically



Naming Cycloalkane Substituents Alphabetically

With two different substituents, number the ring to assign the lower number to the substituents alphabetically.

Begin numbering at the ethyl group.

- **e**thyl group at **C1**
- **m**ethyl group at **C3**

earlier letter ⟶ lower number

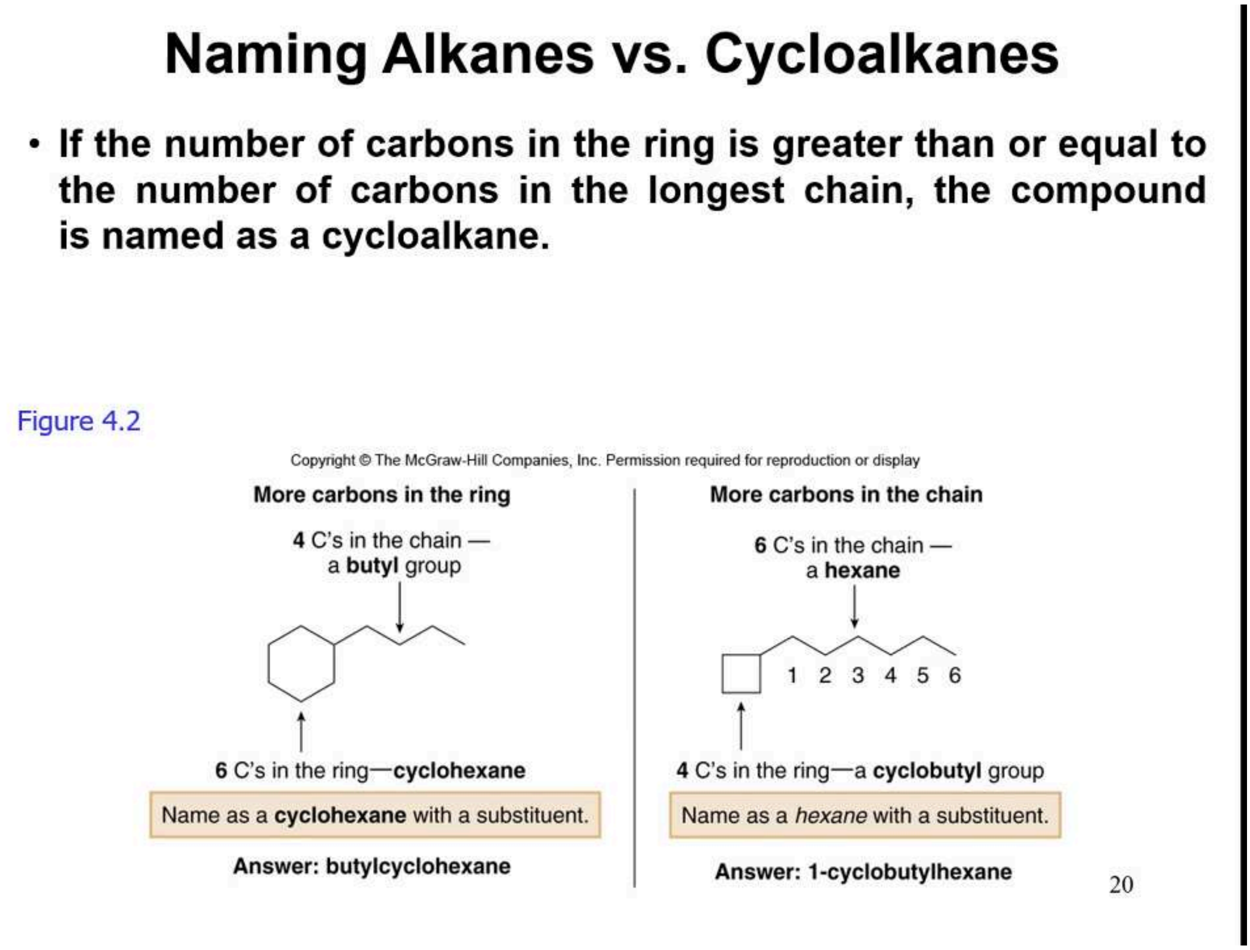
Correct: **1-ethyl-3-methylcyclohexane**

Begin numbering at the methyl group.

- **m**ethyl group at **C1**
- **e**thyl group at **C3**

Incorrect: 3-ethyl-1-methylcyclohexane

If the number of carbons in the ring is greater than or equal to the number of carbons in the longest chain, the compound is named as a cycloalkane.
If there are more carbons in the chain, the compound is named as an alkane.



Naming Alkanes vs. Cycloalkanes

- **If the number of carbons in the ring is greater than or equal to the number of carbons in the longest chain, the compound is named as a cycloalkane.**

Figure 4.2

More carbons in the ring

4 C's in the chain — a **butyl** group

6 C's in the ring—**cyclohexane**

Name as a **cyclohexane** with a substituent.

Answer: butylcyclohexane

More carbons in the chain

6 C's in the chain — a **hexane**

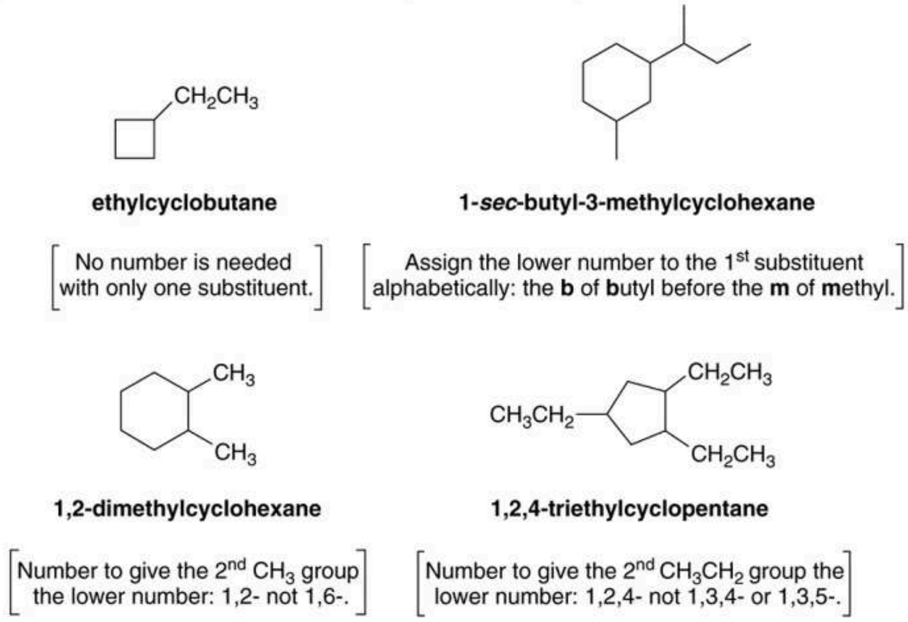
4 C's in the ring—a **cyclobutyl** group

Name as a *hexane* with a substituent.

Answer: 1-cyclobutylhexane

Examples of Naming Cycloalkanes

Figure 4.3



ethylcyclobutane

No number is needed with only one substituent.

1-*sec*-butyl-3-methylcyclohexane

Assign the lower number to the 1st substituent alphabetically: the **b** of **b**utyl before the **m** of **m**ethyl.

1,2-dimethylcyclohexane

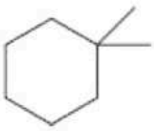
Number to give the 2nd CH_3 group the lower number: 1,2- not 1,6-.

1,2,4-triethylcyclopentane

Number to give the 2nd CH_3CH_2 group the lower number: 1,2,4- not 1,3,4- or 1,3,5-.

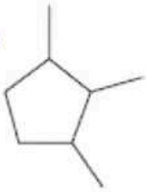
Name the following compounds.

a.



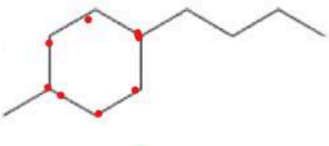
1,1-dimethyl cyclohexane

b.



1,2,3- trimethyl pentane

c.



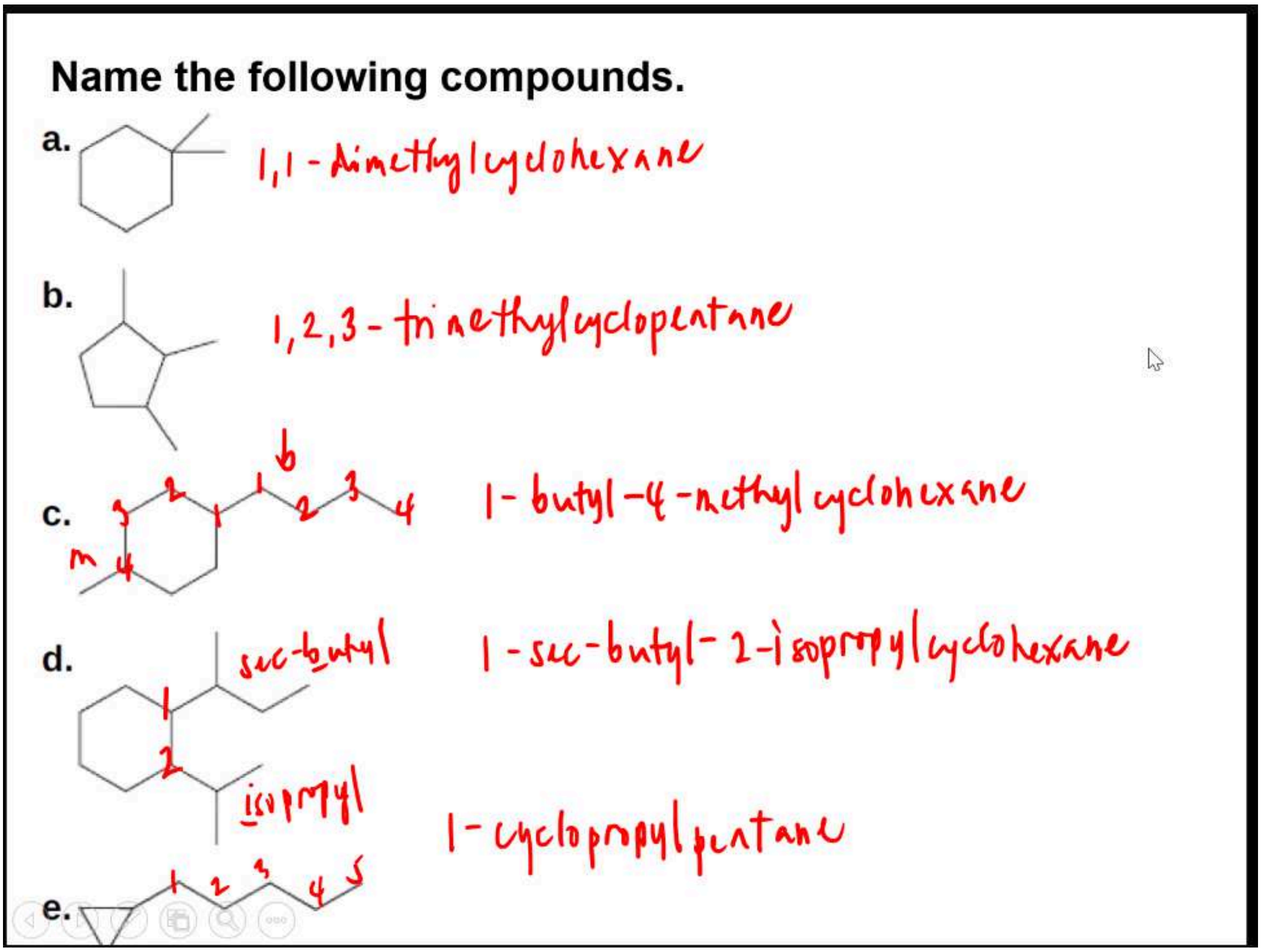
1-butyl-4-methylcyclohexane

d.

1-sec-butyl-2-isopropylcyclohexane

e.

1-cyclopropyl pentane



Name the following compounds.

a. 1,1-dimethylcyclohexane

b. 1,2,3-trimethylcyclopentane

c. 1-butyl-4-methylcyclohexane

d. 1-sec-butyl-2-isopropylcyclohexane

e. 1-cyclopropylpentane

some organic compounds are identified using common names that do not follow the IUPAC system of nomenclature
many of these names were given long ago before the iupac system was adopted and stilla re widely used
additionally some names are descriptive of shape and structure like those below

PROPERTIES OF ALKANES

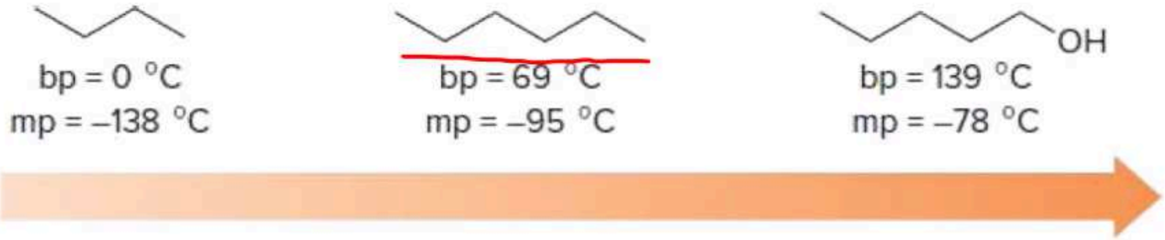
alkanes only contain C-C AND C-H non polar bonds
only exhibit weak van der waals forces
this affects solubility and boilking point and melting point characteristics of alkanes

alkanes are soluble in organic solvenets
alkanes are insoluble in water.

alkanes have low bps and mps compared to polar compounds of comparable size
bp and mp increase as the number of carbons increase because of increased surface area.

Properties of Alkanes

- Alkanes have low bp's and mp's compared to more polar compounds of comparable size.
- Bp and mp increase as the number of carbons increases because of increased surface area.



bp = 0 °C
mp = –138 °C

bp = 69 °C
mp = –95 °C

bp = 139 °C
mp = –78 °C

Increasing strength of intermolecular forces
Increasing boiling point and melting point

Properties of Alkanes

- The bp of isomers decreases with branching because of decreased surface area.
- Mp increases with increased symmetry.

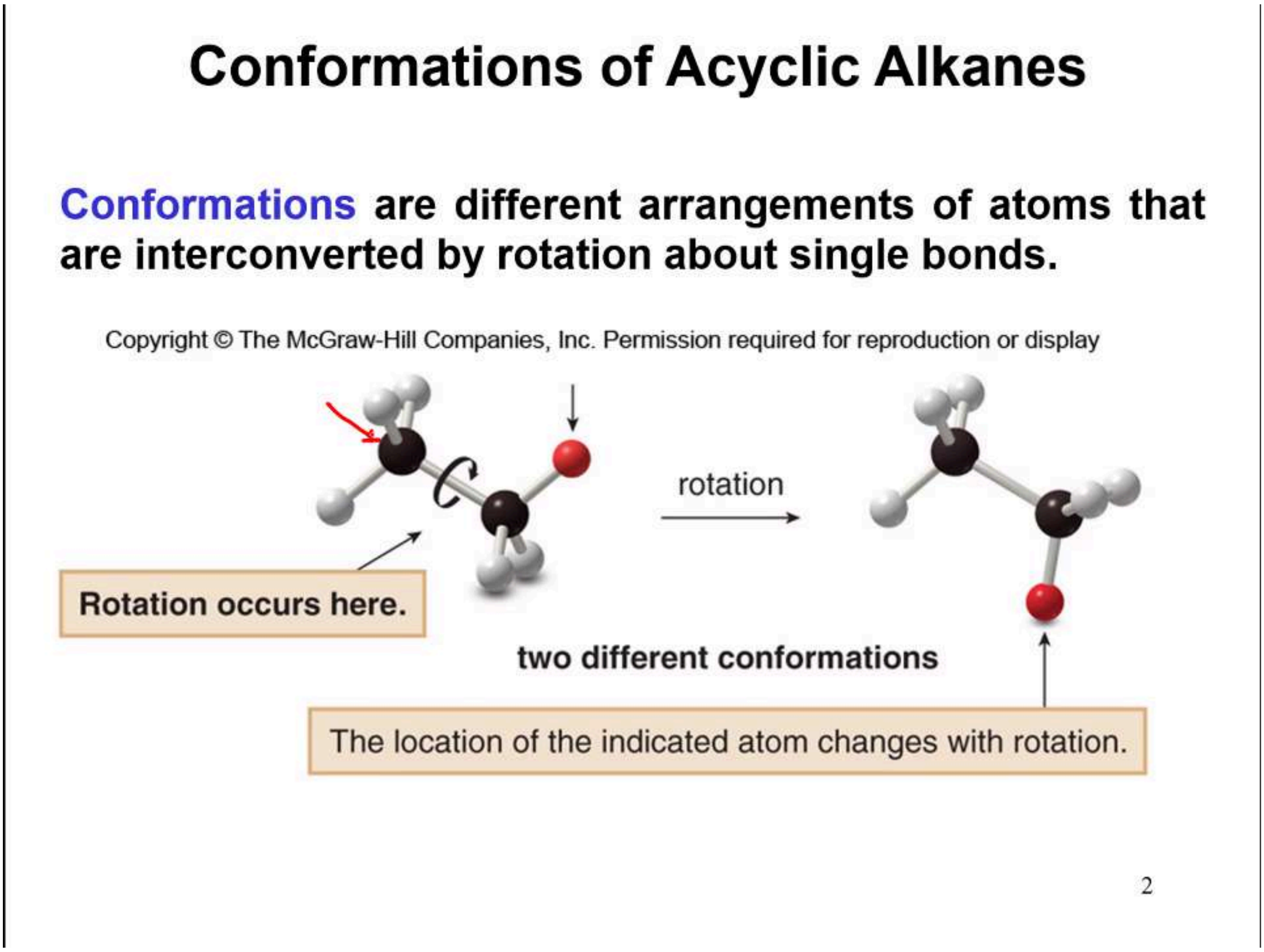
bp = 10 °C
mp = –17 °C

bp = 30 °C
mp = –160 °C

more branching—lower boiling point
more symmetry—higher melting point

Conformations of Acyclic Alkanes

Conformations are different arrangements of atoms that are interconverted by rotation about single bonds (σ bonds)
The arrangement of atoms are the same in terms of connects, the only difference is the rotation about single bonds



Conformations of Acyclic Alkanes

Conformations are different arrangements of atoms that are interconverted by rotation about single bonds.

rotation

Rotation occurs here.

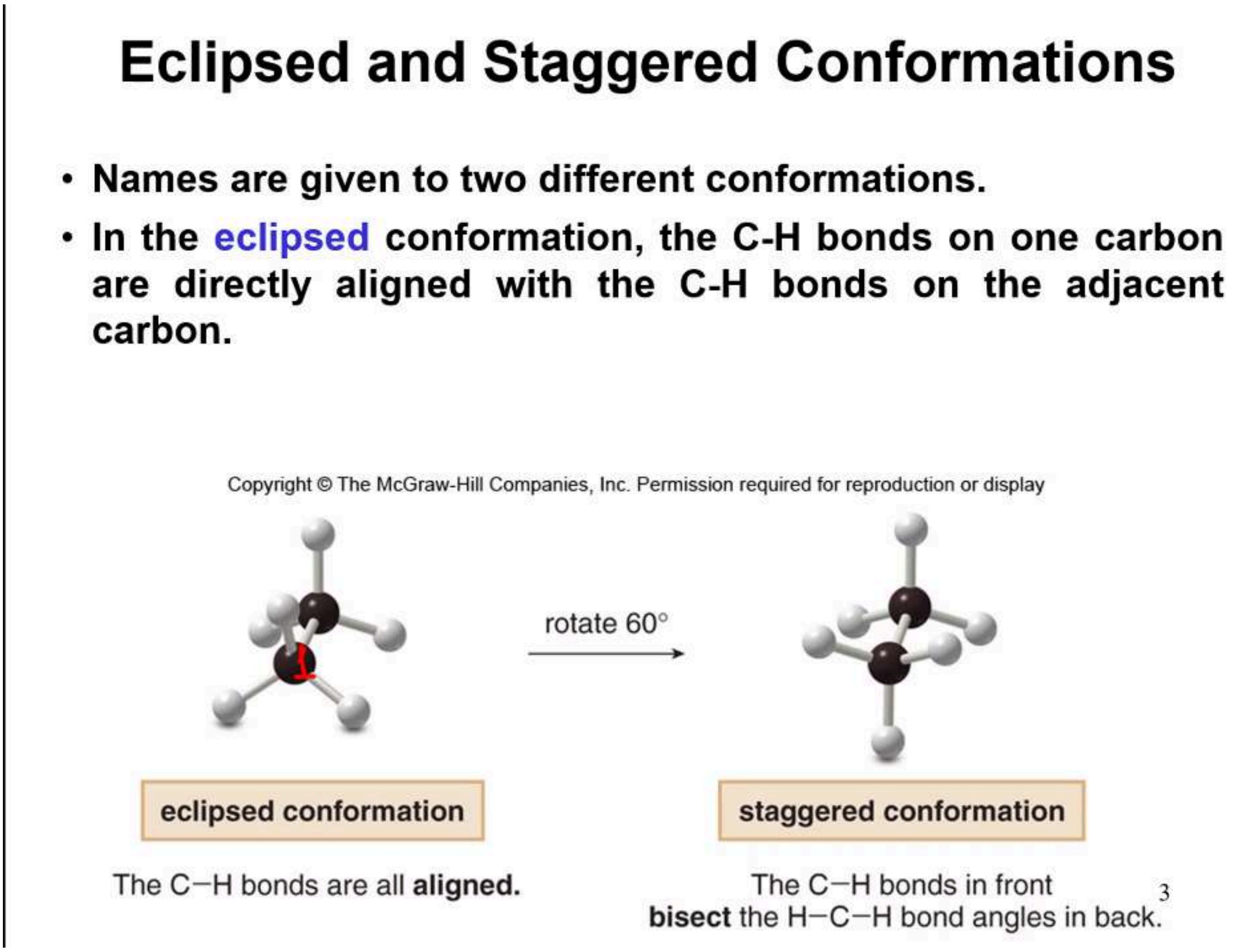
two different conformations

The location of the indicated atom changes with rotation.

2

Eclipsed and Staggered Conformations

Names are given to two different comformations
In the eclipsed conformation, the C-H bonds on one carbon are directlya ligned with the CH bonds on the adjacent carbon.
Think about solar and lunar eclipse.



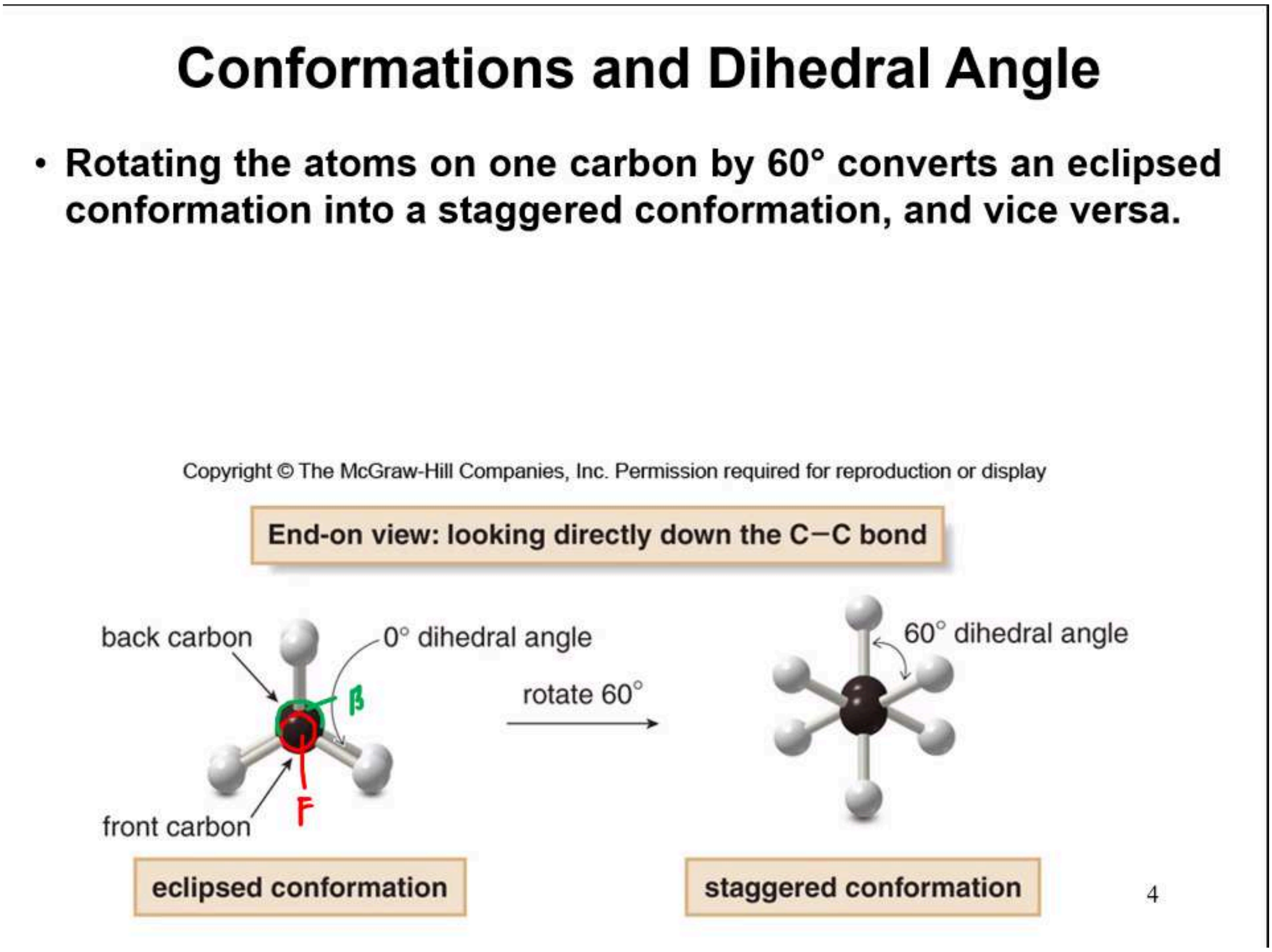
Eclipsed and Staggered Conformations

- **Names are given to two different conformations.**
- **In the eclipsed conformation, the C-H bonds on one carbon are directly aligned with the C-H bonds on the adjacent carbon.**

The C–H bonds are all **aligned.**

The C–H bonds in front **bisect** the H–C–H bond angles in back.

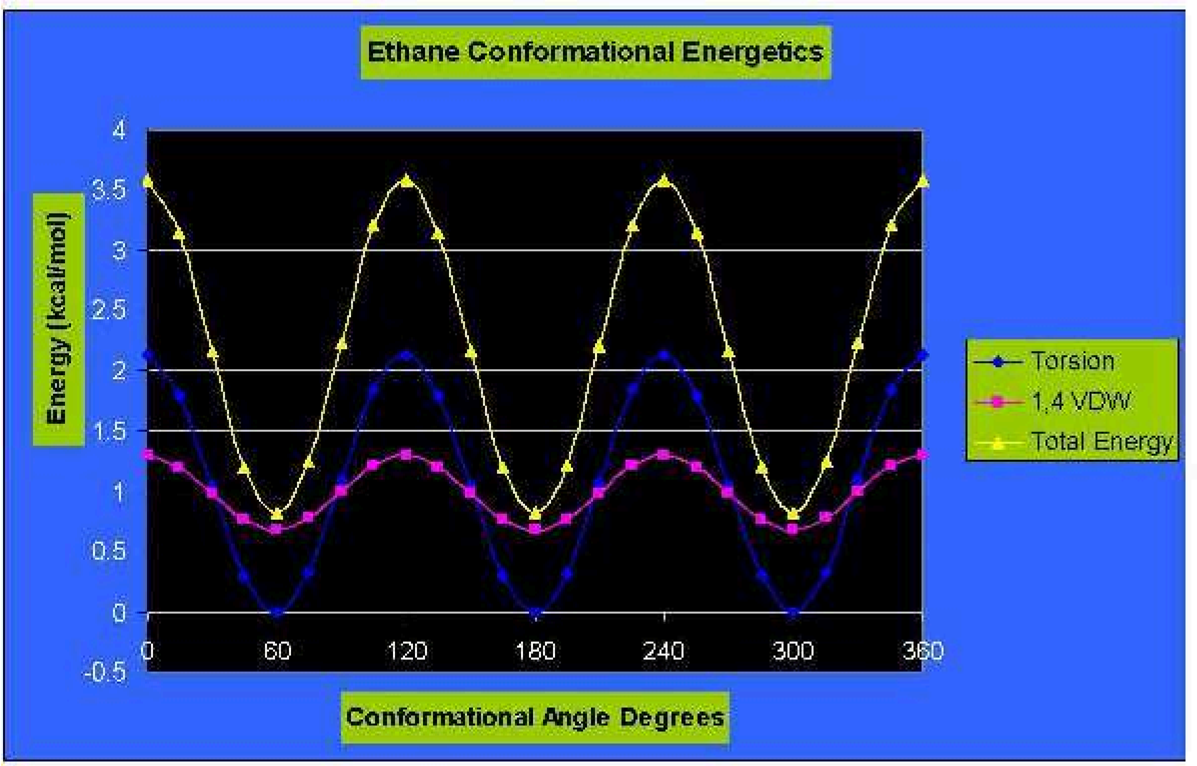
If rotate this eclipsed conformation by 60 degrees, it becomes a staggered conformation.



Conformations and Dihedral Angle

- **Rotating the atoms on one carbon by 60° converts an eclipsed conformation into a staggered conformation, and vice versa.**

staggered conformation - all hydrogens are equally spaced from each other.

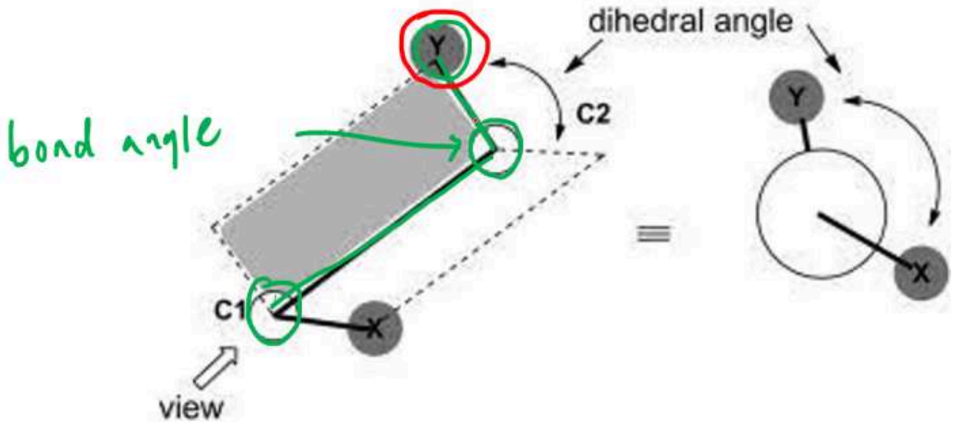


The eclipsed conformation of ethane is less stable than the staggered conformation. Energies for these rotations are measured using Chem 3D, drawing an ethane molecule and minimizing its energy will start it in the staggered conformation. The staggered conformation is the most stable of all possible conformations of ethane, since the angles between C-H bonds on the front and rear carbons are maximized which minimizes the energy. The Total Energy is visualized on the graph by the green curve. The minimums can be seen on the graph at 60, 180 and 300 degrees. In the eclipsed form, the electron densities on the C-H bonds are closer together than they are in the staggered form. When two C-H bonds are brought into a dihedral angle of zero degrees, their electron clouds experience repulsion, which raises the energy of the molecule. The eclipsed conformation of ethane has three such C-H eclipsing interactions, they can be seen on the graph at 0/360, 120, 300 degrees.

what if two carbons are bonded to different numbers of hydrogen-
not just simply hydrogen but can be bonded to other groups so can be
carbon is tetrahedral so its tetravalent so its always bound to 4 bonds usually

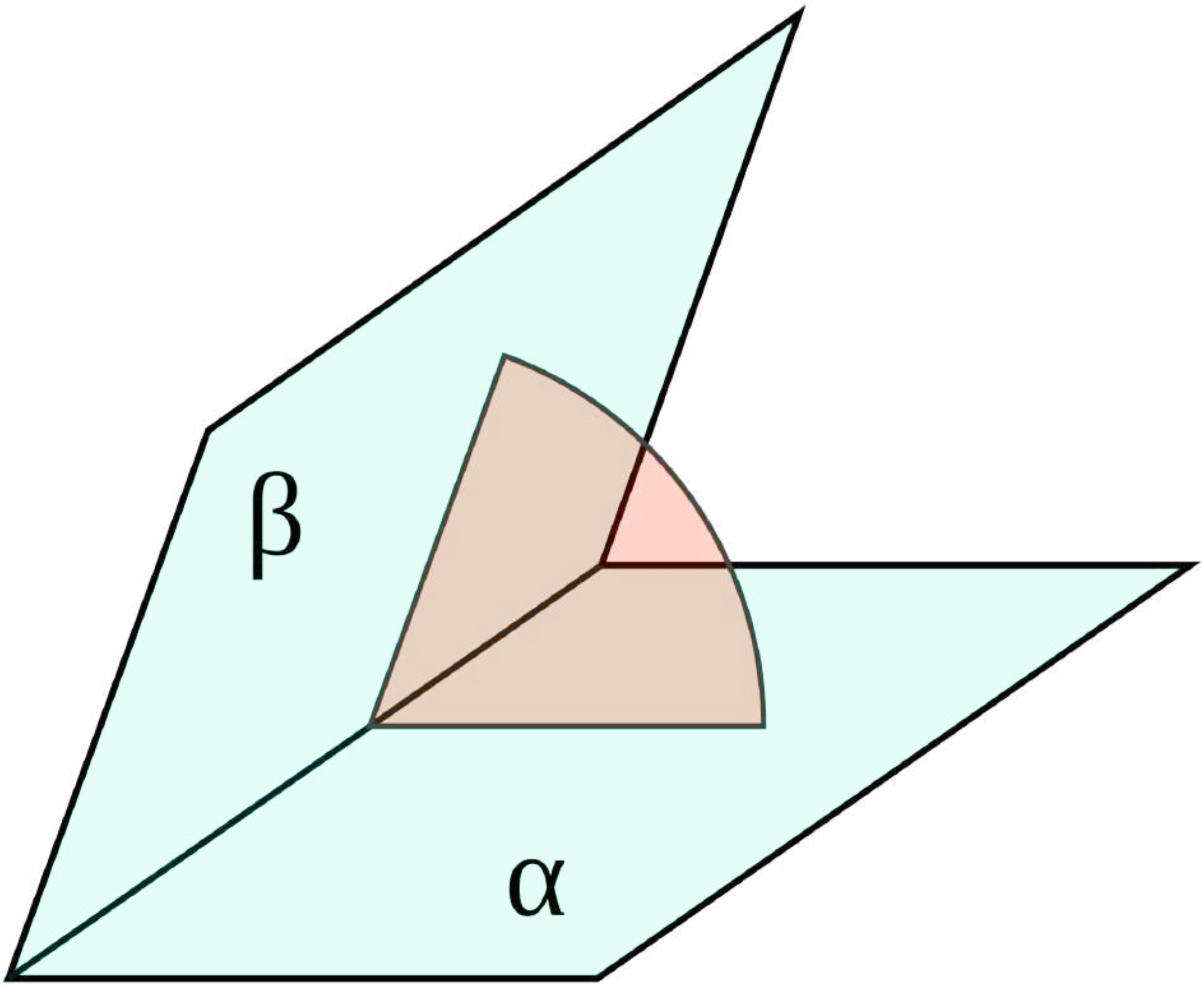
60 degrees = makes arrangement equally spaced. could be 45 or 30 degrees but 60 degrees it is equally spaced. this 60 degree arrangement is usually very stable or very unstable?

Dihedral Angle



let C1 = C2 then dihedral angle is the angle of Y and X.

is the angle between two intersecting planes or half-planes. It is a plane angle formed on a third plane, perpendicular to the line of intersection between the two planes or the common edge between the two half-planes. In higher dimensions, a dihedral angle represents the angle between two hyperplanes. In chemistry, it is the clockwise angle between half-planes through two sets of three atoms, having two atoms in common.



End on representations for conformations are commonly drawn using a convention called a newman projection.

- quiz, give you a structure, point a carbon as one in front and one in front, then draw the rest in newman projection.

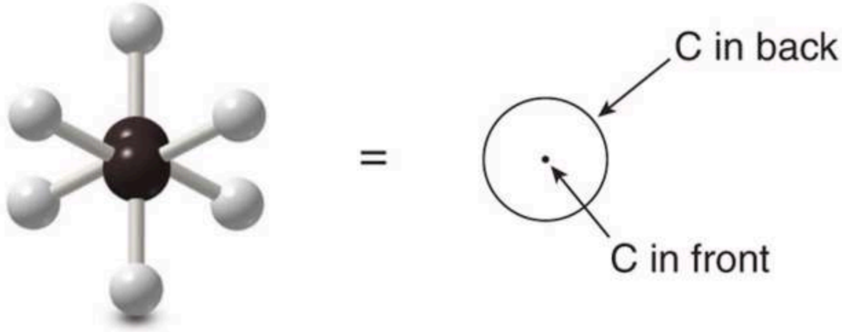
1. look directly down on the C-C bond, draw a circle with a dot in the center to represent the carbons of the C-C bond.
2. Draw the bonds on the front C as three lines meeting at the center of the cirlce
3. Draw the bonds on the back C as three lines coming out of the edge of the circle.

Newman Projections

- End-on representations for conformations are commonly drawn using a convention called a Newman projection.

HOW TO Draw a Newman Projection:

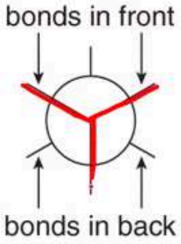
Step [1] Look directly down the C-C bond (end-on), and draw a circle with a dot in the center to represent the carbons of the C-C bond.



Completing a Newman Projection

Step 2. Draw in the bonds.

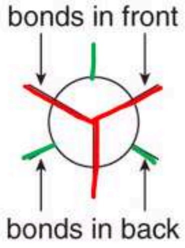
- Draw the bonds on the front C as three lines meeting at the center of the circle.



Completing a Newman Projection

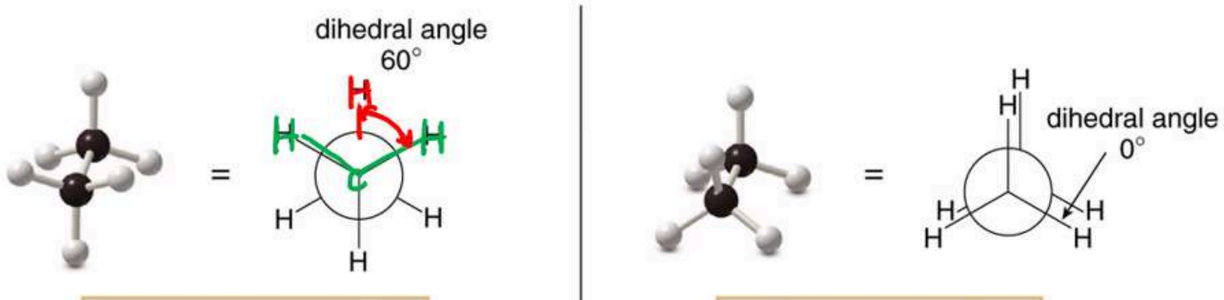
Step 2. Draw in the bonds.

- **Draw the bonds on the front C as three lines meeting at the center of the circle.**
- **Draw the bonds on the back C as three lines coming out of the edge of the circle.**



Newman Projections - Ethane

Figure 4.6

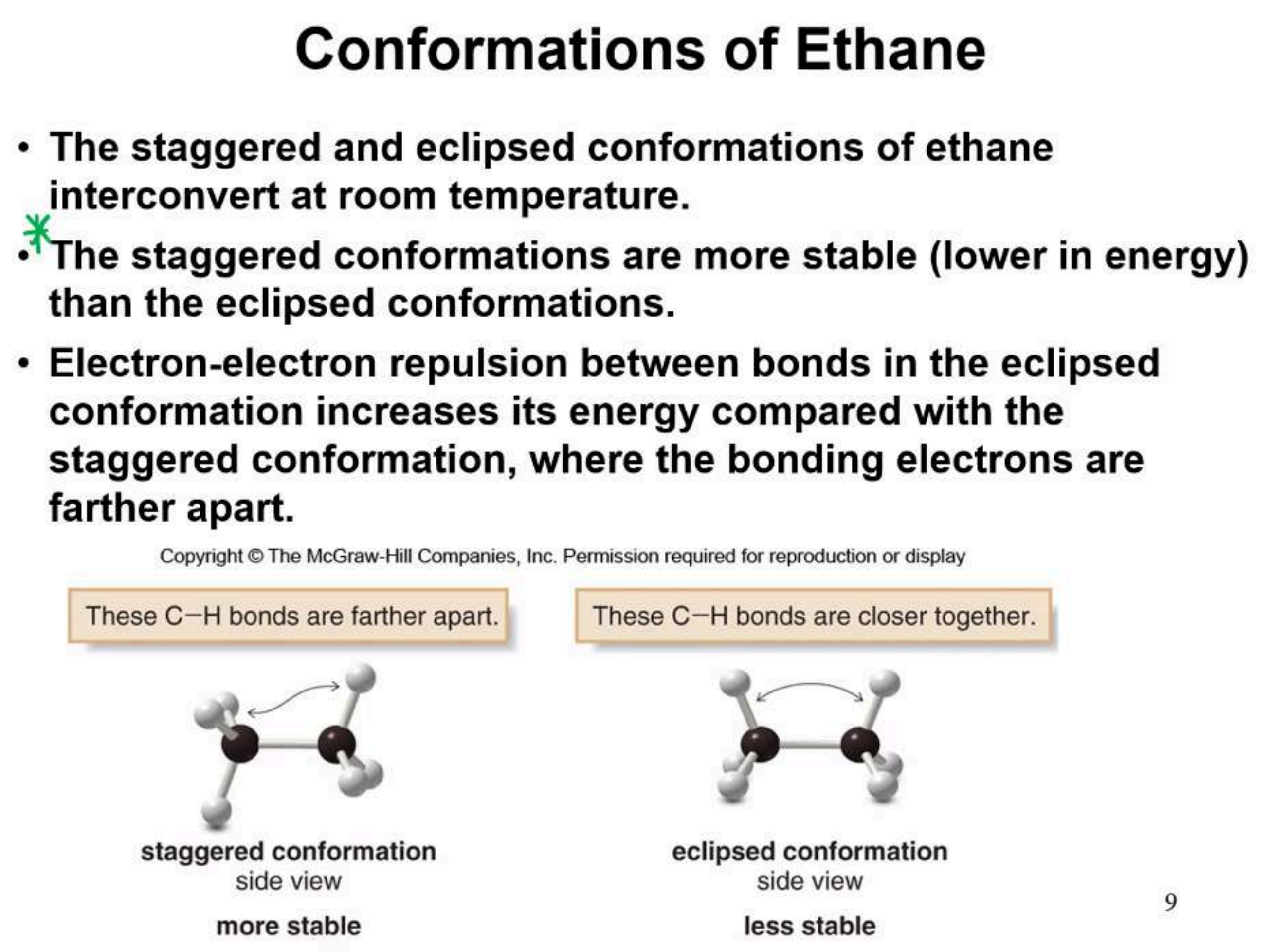


staggered conformation

eclipsed conformation

the staggered and eclipsed conformations of ethane interconvert at room temperature

the staggered conformations are more stable (lower in energy) than the eclipsed conformations.



Conformations of Ethane

- The staggered and eclipsed conformations of ethane interconvert at room temperature.
- * The staggered conformations are more stable (lower in energy) than the eclipsed conformations.
- Electron-electron repulsion between bonds in the eclipsed conformation increases its energy compared with the staggered conformation, where the bonding electrons are farther apart.

These C–H bonds are farther apart.

These C–H bonds are closer together.

staggered conformation
side view
more stable

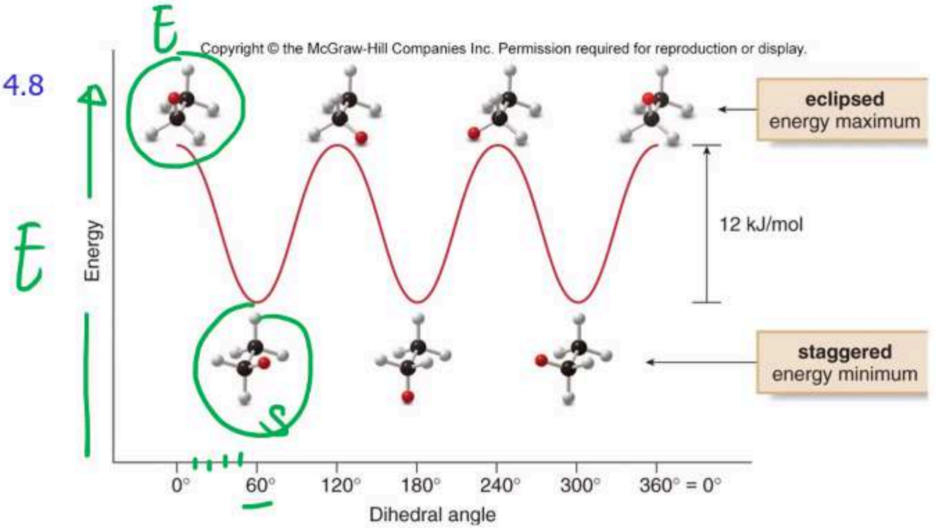
eclipsed conformation
side view
less stable

60 degrees= atoms would be equally far away

Torsional Energy of Ethane

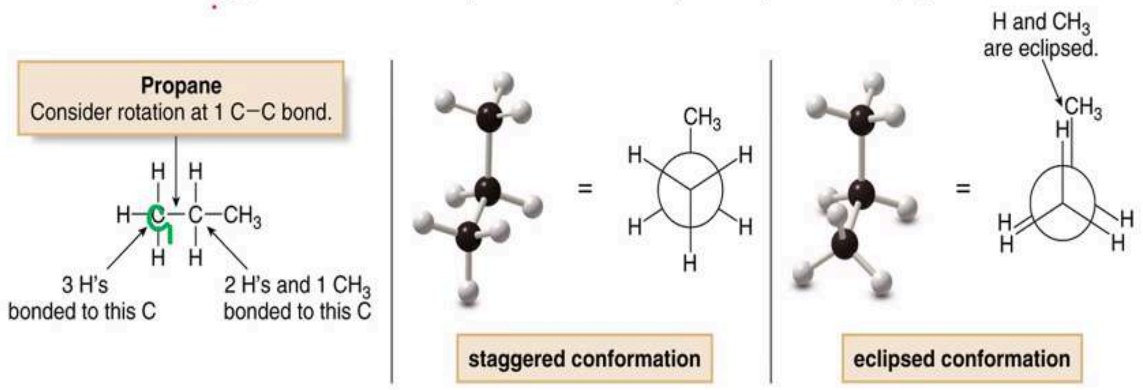
- The difference in energy between staggered and eclipsed conformers is ~3 kcal/mol, with each eclipsed C-H bond contributing 1 kcal/mol.

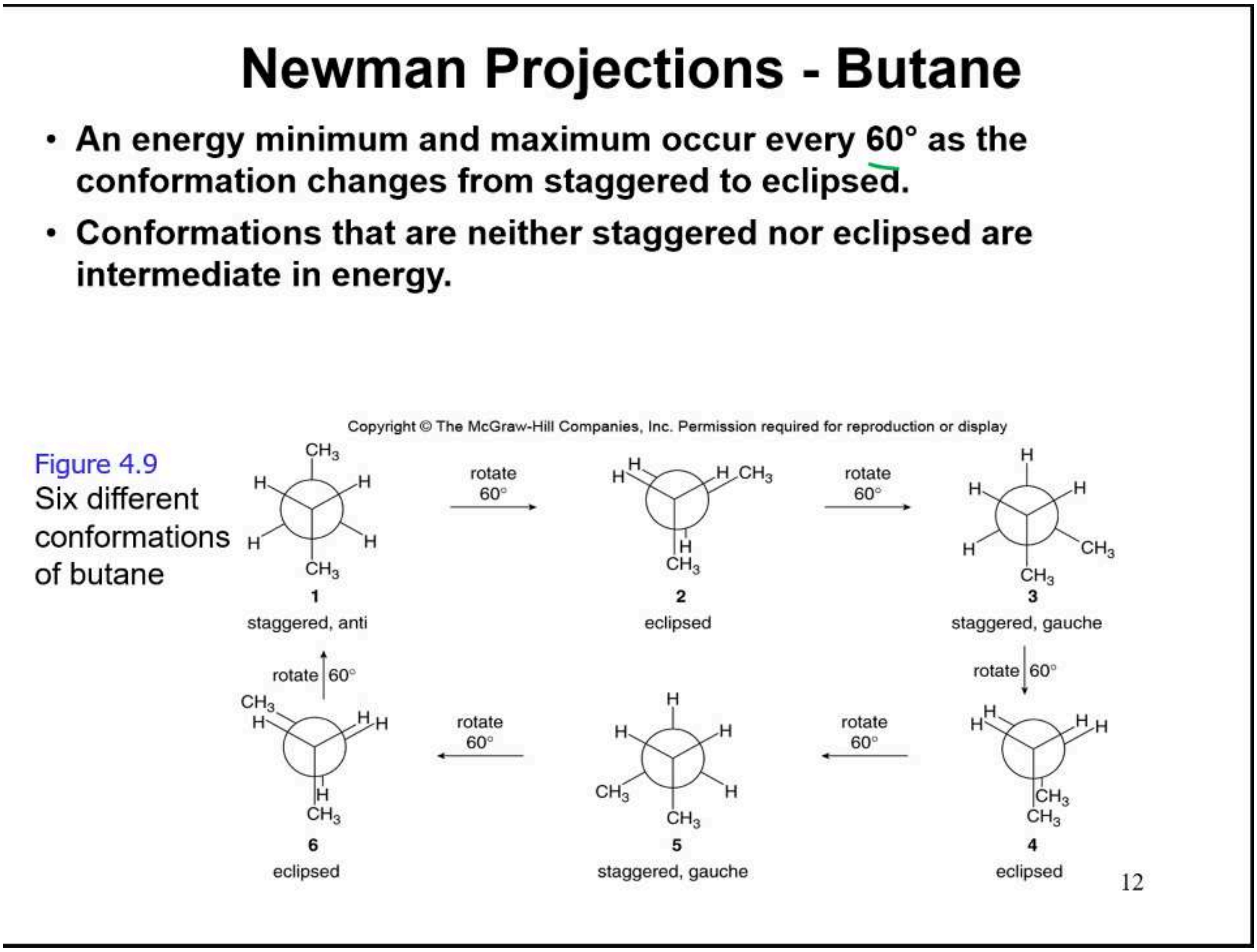
Figure 4.8



Newman Projections - Propane

Figure 4.7





Newman Projections - Butane

- An energy minimum and maximum occur every 60° as the conformation changes from staggered to eclipsed.
- Conformations that are neither staggered nor eclipsed are intermediate in energy.

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Figure 4.9 Six different conformations of butane

1 staggered, anti

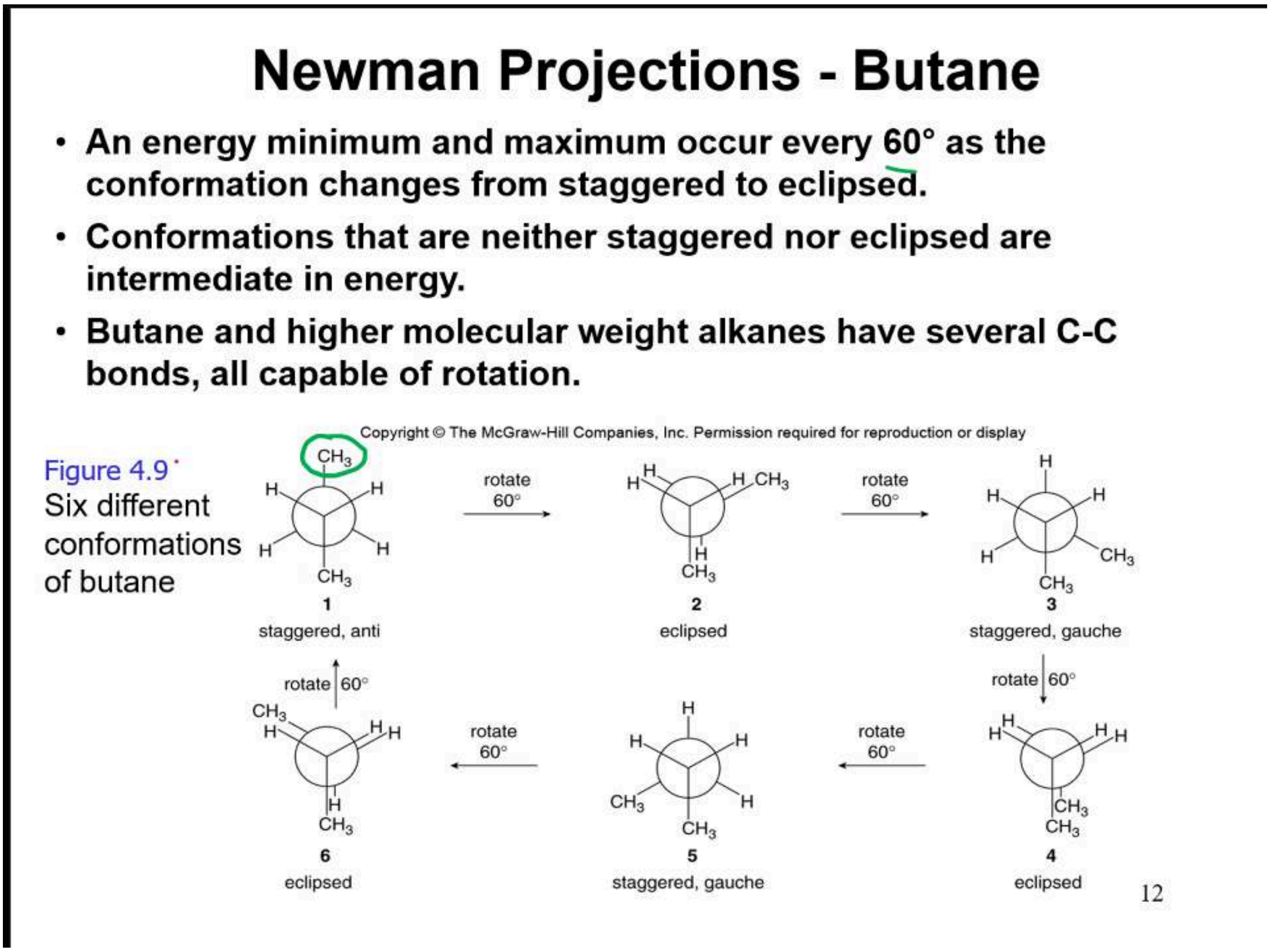
2 eclipsed

3 staggered, gauche

6 eclipsed

5 staggered, gauche

4 eclipsed



Newman Projections - Butane

- An energy minimum and maximum occur every 60° as the conformation changes from staggered to eclipsed.
- Conformations that are neither staggered nor eclipsed are intermediate in energy.
- Butane and higher molecular weight alkanes have several C-C bonds, all capable of rotation.

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Figure 4.9 Six different conformations of butane

1 staggered, anti

2 eclipsed

3 staggered, gauche

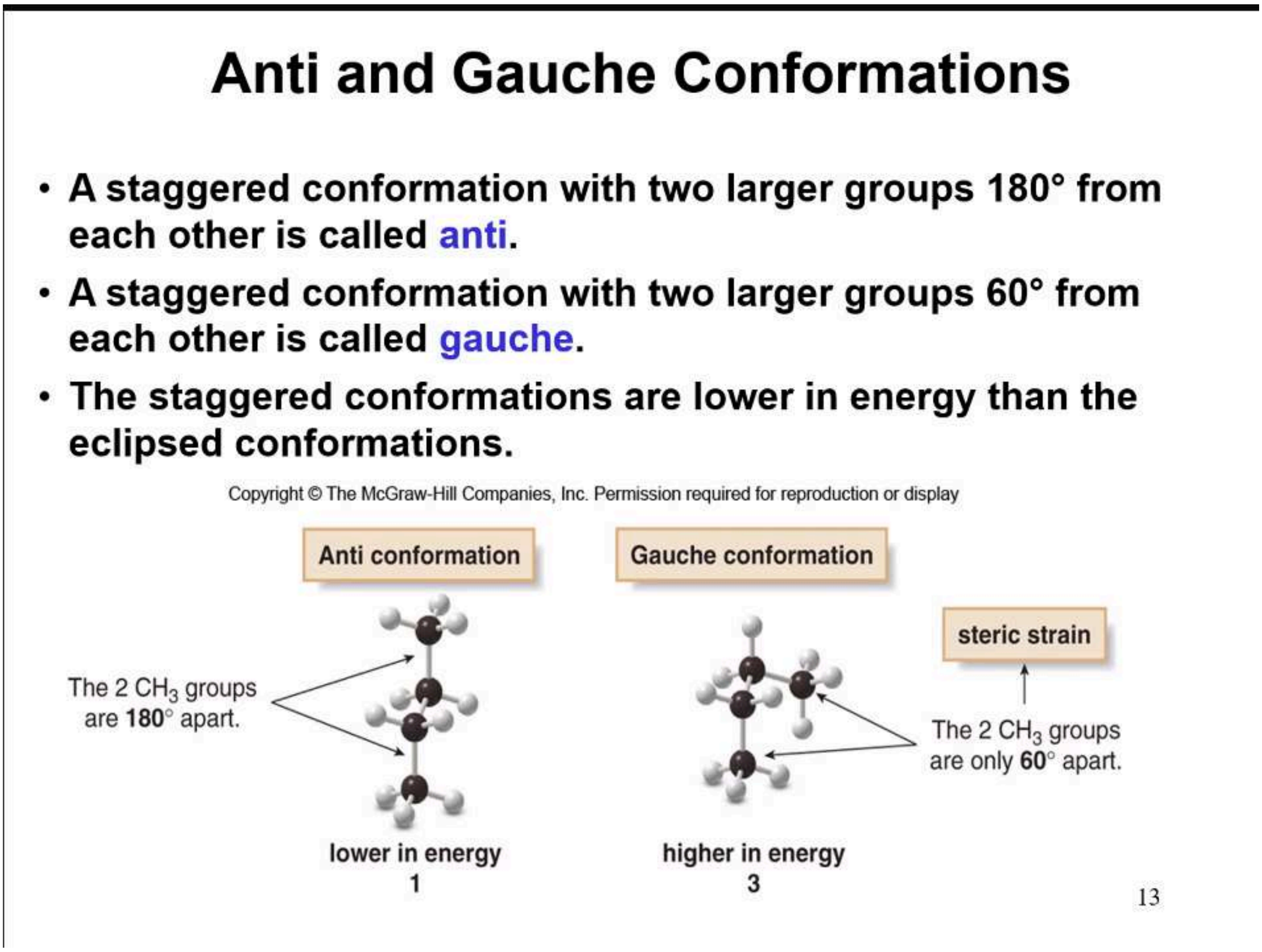
6 eclipsed

5 staggered, gauche

4 eclipsed

staggered anti, the bulky methyls are as far away from each other.

for staggered gauche, methyl groups are just 60 degrees apart.



Anti and Gauche Conformations

- **A staggered conformation with two larger groups 180° from each other is called anti.**
- **A staggered conformation with two larger groups 60° from each other is called gauche.**
- **The staggered conformations are lower in energy than the eclipsed conformations.**

Anti conformation

The 2 CH_3 groups are **180°** apart.

lower in energy
1

Gauche conformation

steric strain

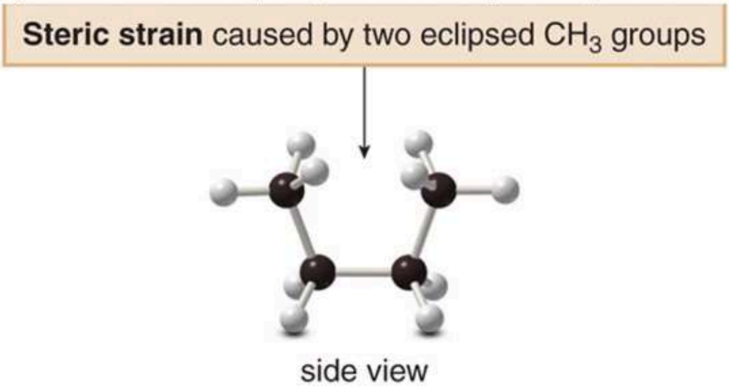
The 2 CH_3 groups are only **60°** apart.

higher in energy
3

torsional strain from eclipsing
steric strain is an increase in energy resulting when non bonded atoms are forced too close to one another
relative energies of the individual staggered conformations on their steric strain
gauche confromations are higher in energy due to steric strain compared to anti conformations

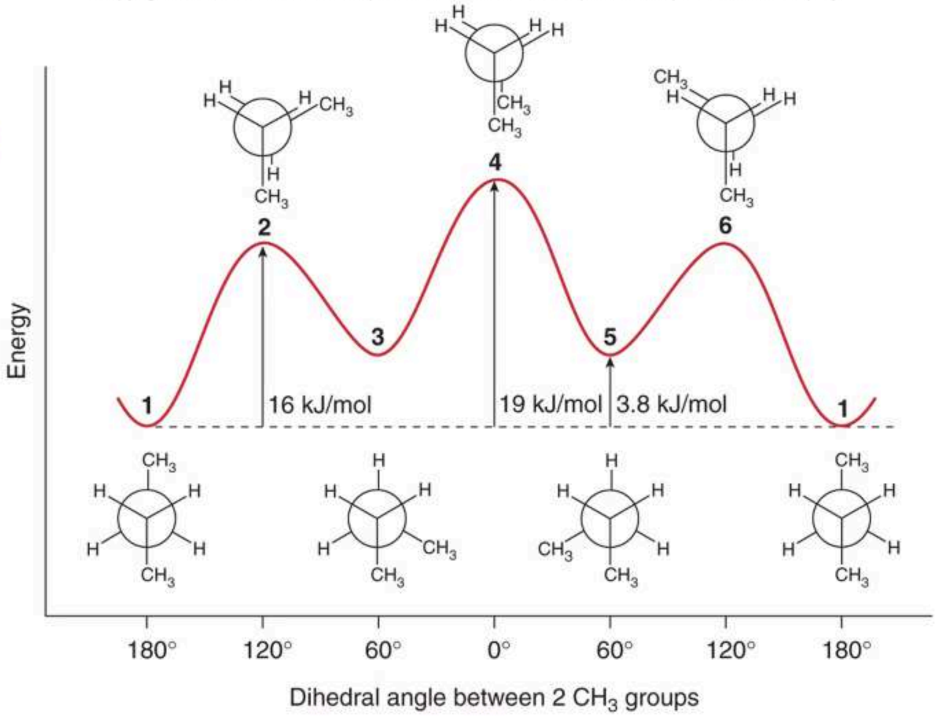
Steric Strain

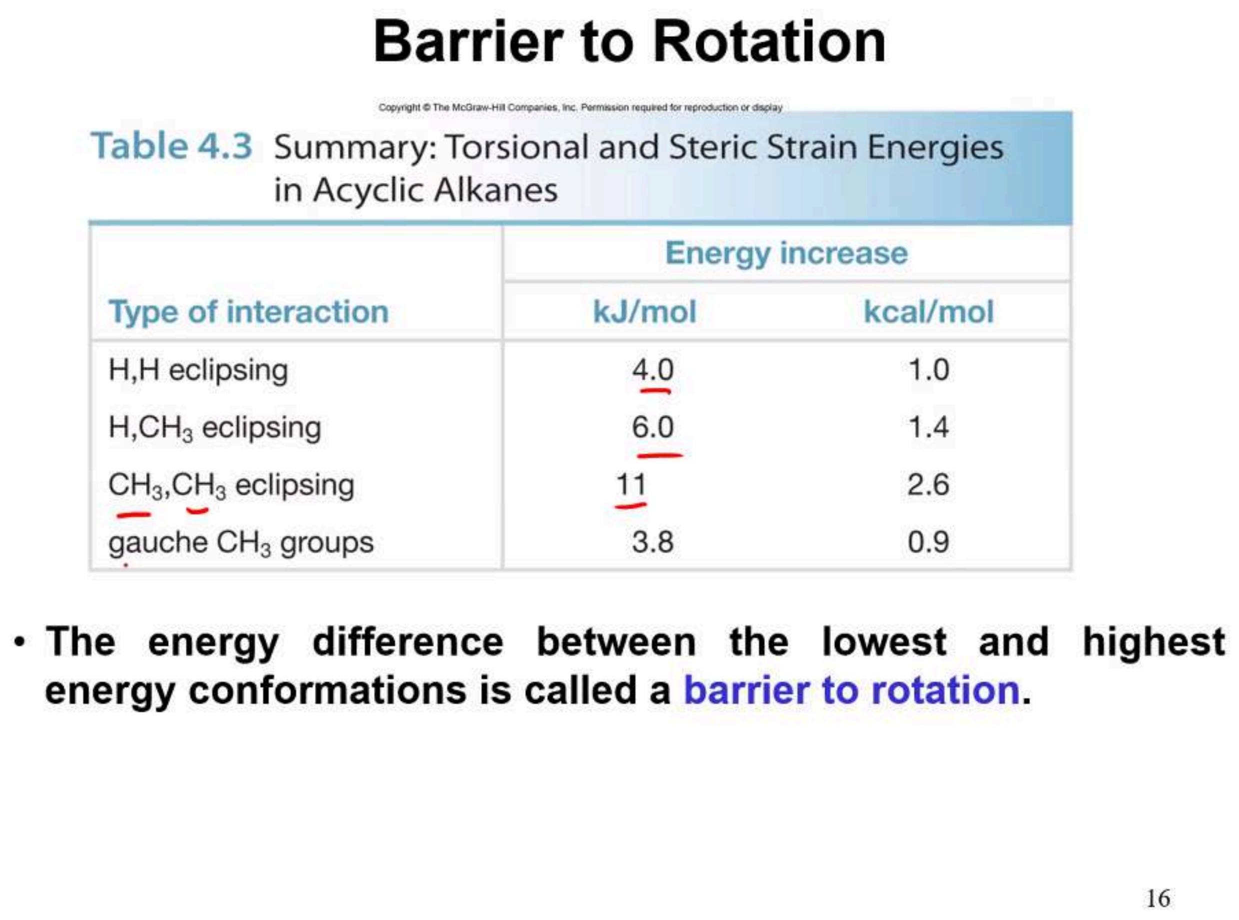
- The relative energies of the individual staggered conformations depend on their steric strain.



Conformation and Energy of Butane

Figure 4.10





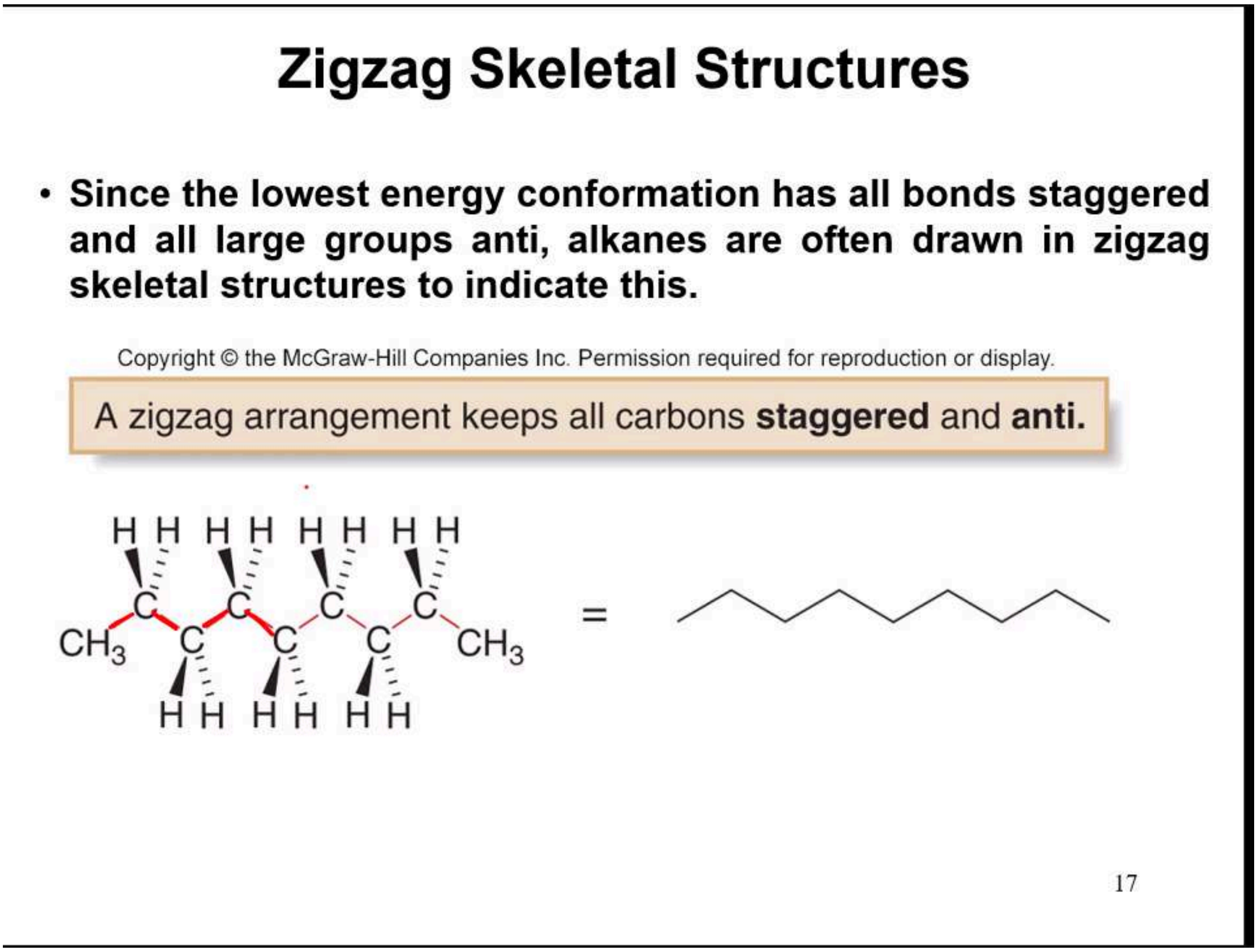
Barrier to Rotation

Table 4.3 Summary: Torsional and Steric Strain Energies in Acyclic Alkanes

Type of interaction	Energy increase	
	kJ/mol	kcal/mol
H,H eclipsing	4.0	1.0
H,CH_3 eclipsing	6.0	1.4
CH_3,CH_3 eclipsing	11	2.6
gauche CH_3 groups	3.8	0.9

- **The energy difference between the lowest and highest energy conformations is called a barrier to rotation.**

Since the lowest energy conformation has all bonds staggered and all large groups atni, alkanes are often drawn in zigzag skeletal strutures to indicate this.
A zigzag arrangement keeps all carbons staggered and anti.



Zigzag Skeletal Structures

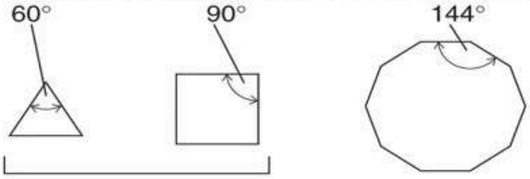
- **Since the lowest energy conformation has all bonds staggered and all large groups anti, alkanes are often drawn in zigzag skeletal structures to indicate this.**

A zigzag arrangement keeps all carbons **staggered** and **anti.**

besides torsional strain and steric chain, the conformations of cycloalkanes are also affect by angle strain

angle strain is an increase in energy when bond angles deviate from the optimum tetrahedral angleof 109.5 deg
cyclockalnes with more than three c atoms are puckered to reduce strain

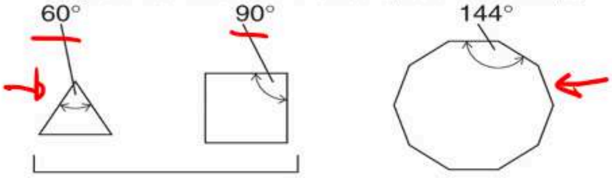
Three to Ten Carbon Cycloalkanes



small internal angles
angle strain

large internal angles
angle strain

Three to Ten Carbon Cycloalkanes

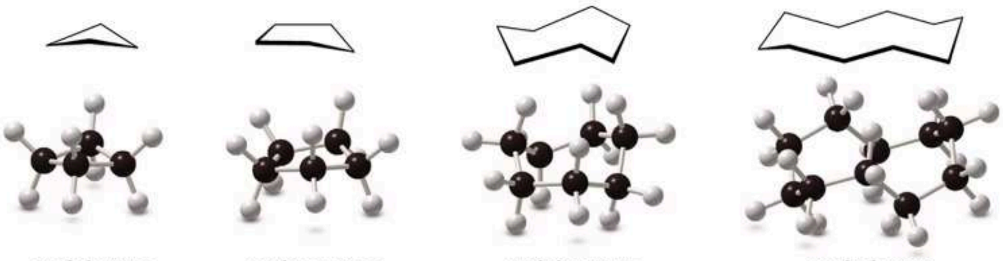


small internal angles
angle strain

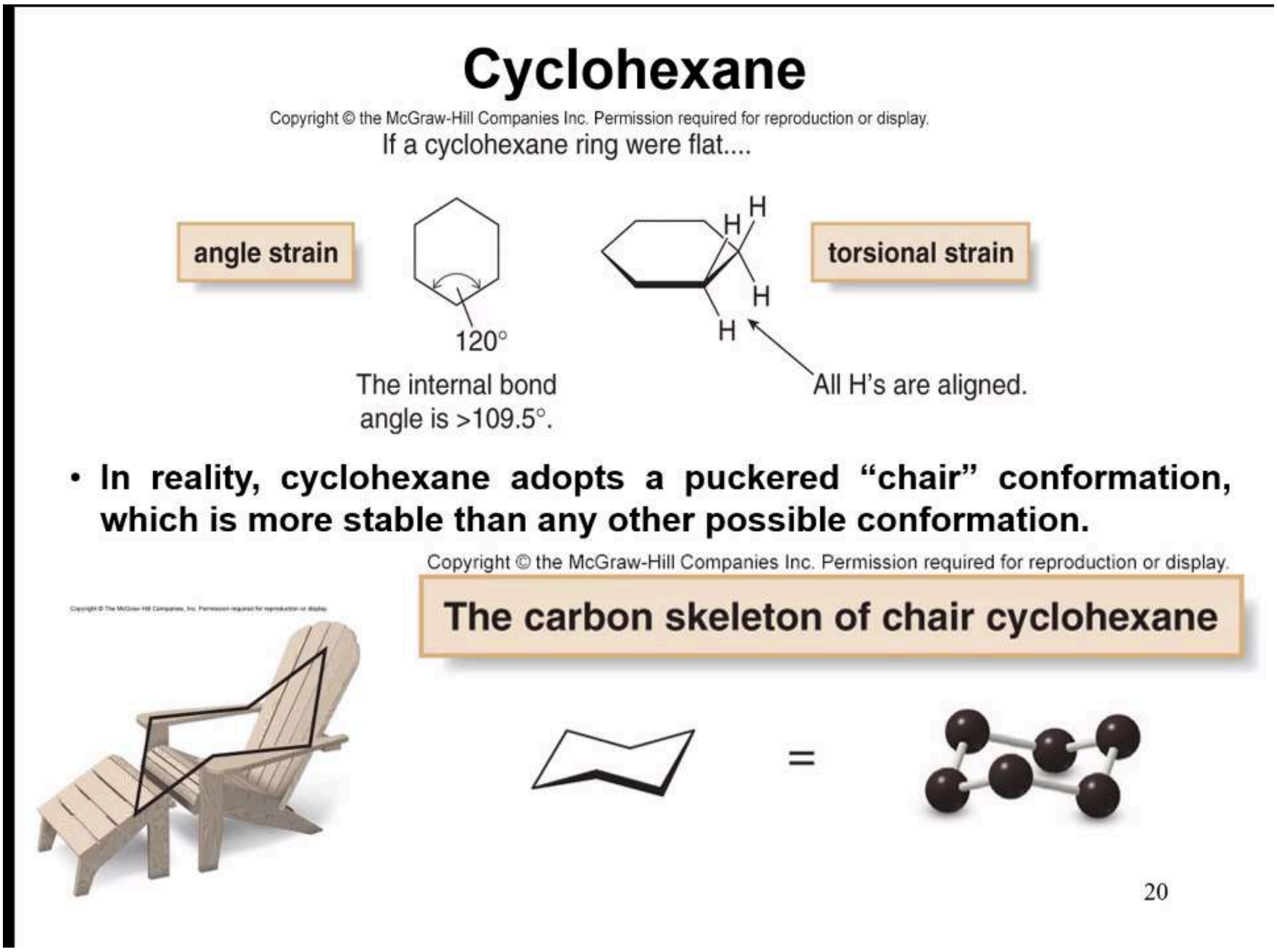
large internal angles
angle strain

Cycloalkanes distort their shapes to alleviate angle and torsional strain.

Figure 4.11



Cyclohexane



Cyclohexane

If a cyclohexane ring were flat....

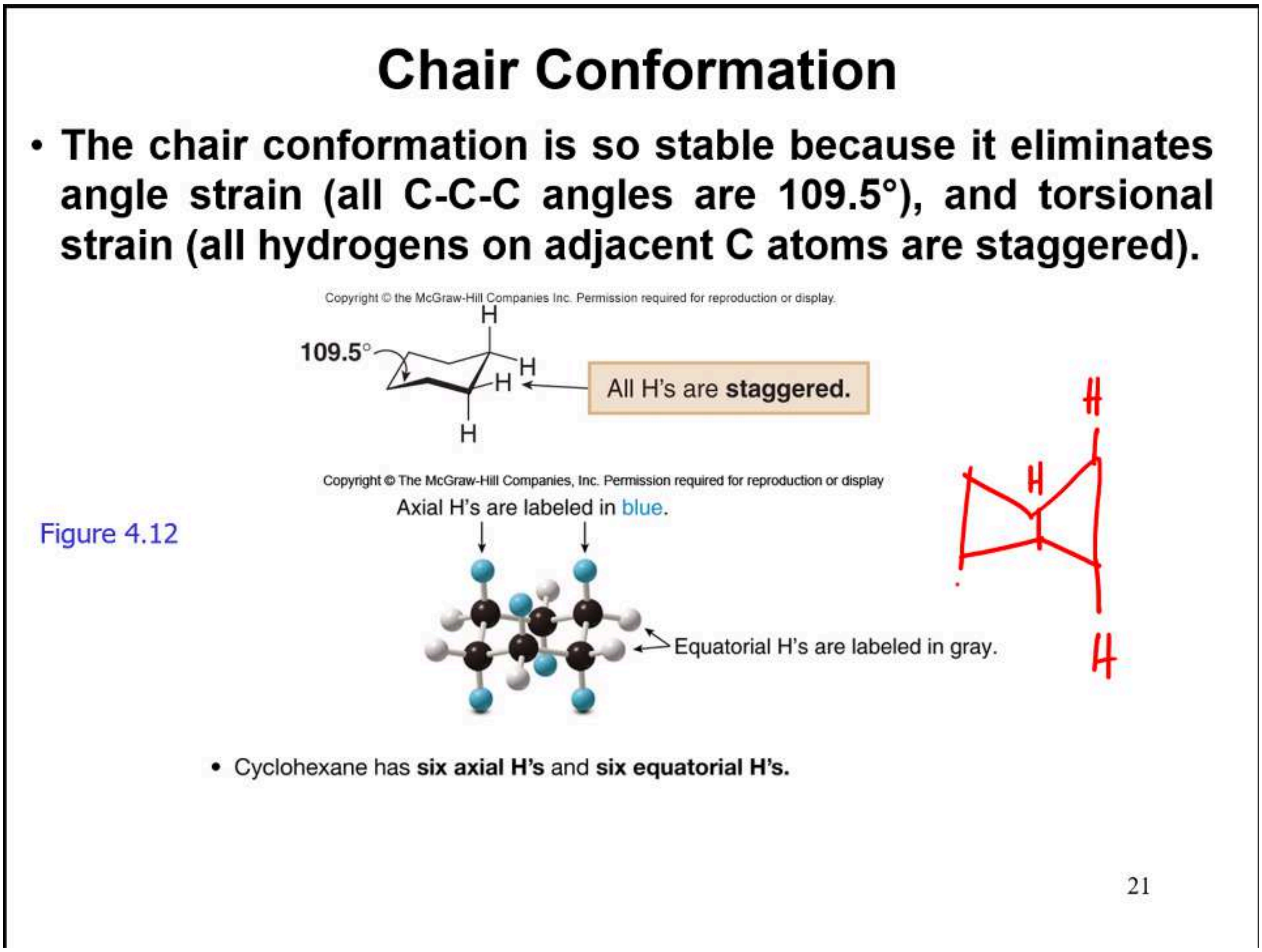
The internal bond angle is >109.5°.

All H's are aligned.

- **In reality, cyclohexane adopts a puckered "chair" conformation, which is more stable than any other possible conformation.**

The carbon skeleton of chair cyclohexane

Chair conformation is so stable because it eliminates all all angle strain, all CCC angles are 109.5, and torsional strain, all hydrogens on adjacent C atoms are staggered.



Chair Conformation

- **The chair conformation is so stable because it eliminates angle strain (all C-C-C angles are 109.5°), and torsional strain (all hydrogens on adjacent C atoms are staggered).**

All H's are **staggered.**

Figure 4.12

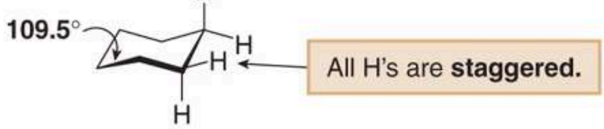
Axial H's are labeled in blue.

Equatorial H's are labeled in gray.

- Cyclohexane has **six axial H's** and **six equatorial H's.**

Chair Conformation

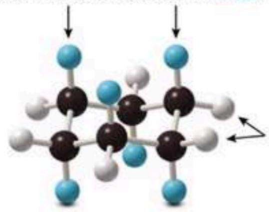
- **The chair conformation is so stable because it eliminates angle strain (all C-C-C angles are 109.5°), and torsional strain (all hydrogens on adjacent C atoms are staggered).**



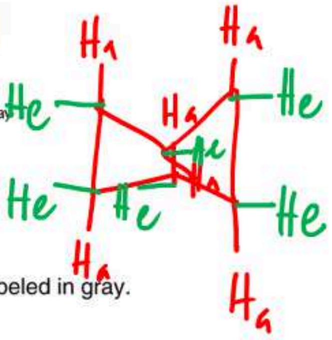
All H's are **staggered.**

Figure 4.12

Axial H's are labeled in blue.



Equatorial H's are labeled in gray.

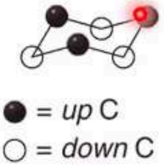


- Cyclohexane has **six axial H's** and **six equatorial H's.**

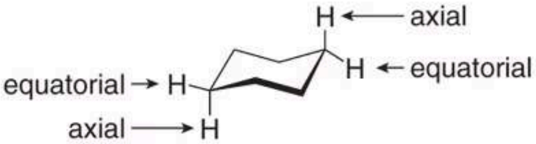
Axial and Equatorial Positions

- **Each C in cyclohexane has two different kinds of hydrogens:**

3 *up* C's and 3 *down* C's



Two kinds of H's

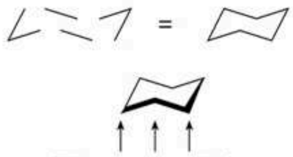


- **Axial** bonds are oriented **above** and **below.**
- **Equatorial** bonds are oriented around the **equator.**

Drawing Cyclohexanes

HOW TO Draw the Chair Form of Cyclohexane

Step [1] Draw the carbon skeleton.



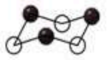
These atoms are in front.

- Draw three parts of the chair: **a wedge, a set of parallel lines,** and **another wedge.**
- Then, join them together.
- The bottom 3 C's come out of the page, and for this reason, bonds to them are often highlighted in bold.

—Continued

HOW TO, continued . . .

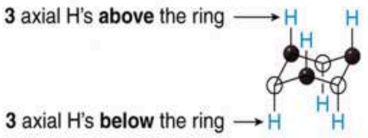
Step [2] Label the *up* C's and *down* C's on the ring.



● = *up* C ○ = *down* C

- There are 3 *up* and 3 *down* C's, and they alternate around the ring.

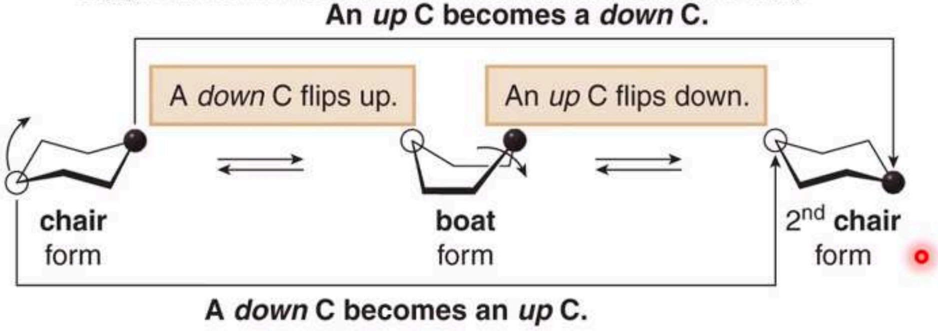
Step [3] Draw in the axial H atoms.



- On an *up* C the axial H is *up.*
- On a *down* C the axial H is *down.*

Conformational Change – Ring-Flipping

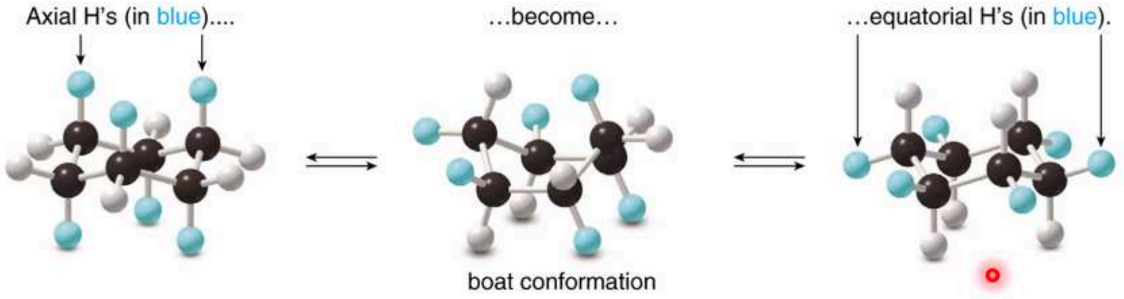
- **Cyclohexanes undergo a conformational change called "ring-flipping."**
  - **As a result of a ring flip, the up carbons become down carbons, and the down carbons become up carbons.**
  - **Axial and equatorial H atoms are also interconverted during a ring-flip; axial H atoms become equatorial H atoms, and equatorial H atoms become axial H atoms.**



Conformational Change – Ring-Flipping

- **There are two possible chair conformations.**
- **The equatorial position has more room than the axial position, so larger substituents are more stable in the equatorial position.**

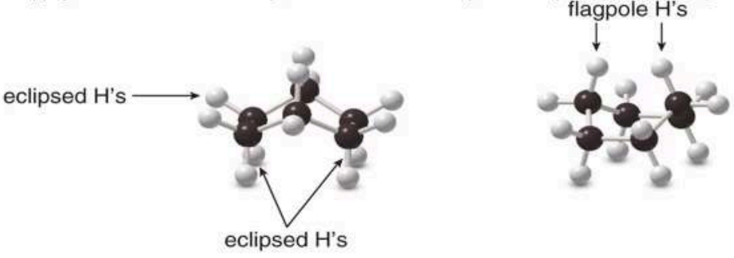
Figure 4.13



Boat Conformation of Cyclohexane

- **Cyclohexane also can exist in a boat conformation.**
- **The boat forms of cyclohexane are 7 kcal/mol less stable than the chair forms.**
- **The boat conformation is destabilized by torsional strain because the hydrogens on the four carbon atoms in the plane are eclipsed.**

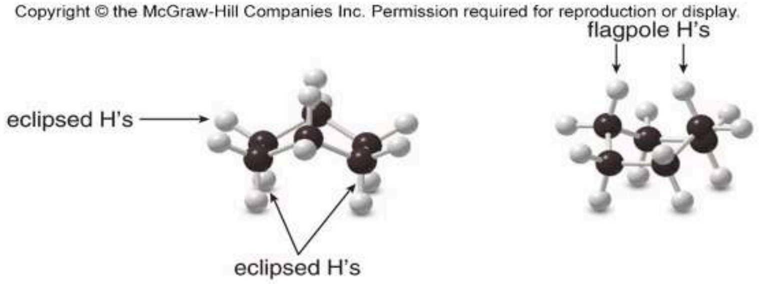
Figure 4.14



Boat Conformation of Cyclohexane

- Cyclohexane also can exist in a boat conformation.
- The boat forms of cyclohexane are 7 kcal/mol less stable than the chair forms.
- The boat conformation is destabilized by torsional strain because the hydrogens on the four carbon atoms in the plane are eclipsed.
- Additionally, there is steric strain because two hydrogens at either end of the boat, the “flag pole” hydrogens, are forced close to each other.

Figure 4.14

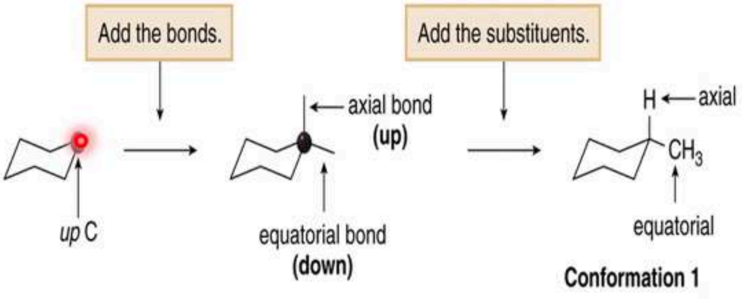


Drawing Substituted Cyclohexanes

HOW TO Draw the Two Conformations for a Substituted Cyclohexane

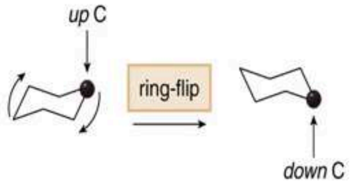
Step [1] Draw one chair form and add the substituents.

- Arbitrarily pick a ring carbon, classify it as an *up* or *down* carbon, and draw the bonds. Each C has one axial and one equatorial bond.
- Add the substituents, in this case H and CH_3, arbitrarily placing one axial and one equatorial. In this example, the CH_3 group is drawn equatorial.
- This forms one of the two possible chair conformations, labeled Conformation **1**.



HOW TO Draw the Two Conformations for a Substituted Cyclohexane

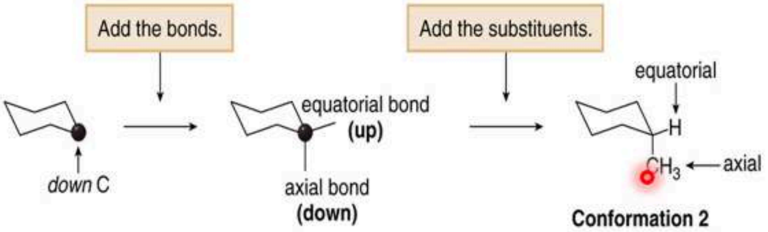
Step [2] Ring-flip the cyclohexane ring.



- Convert *up* C's to *down* C's and vice versa. The chosen *up* C now puckers down.

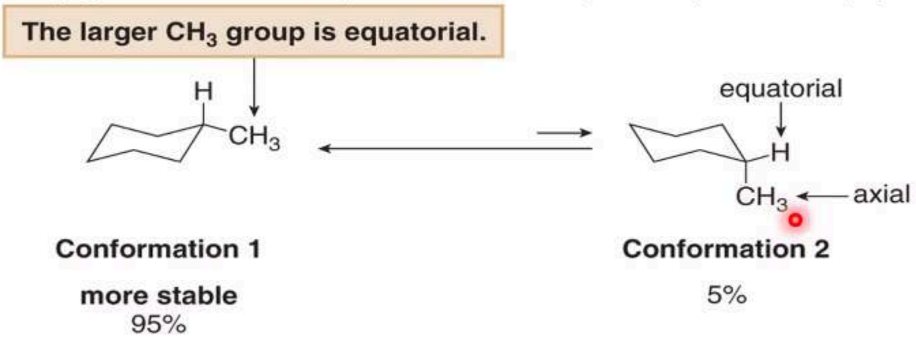
Step [3] Add the substituents to the second conformation.

- Draw axial and equatorial bonds. On a *down* C the axial bond is *down.*
- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The equatorial methyl becomes axial.
- This forms the other possible chair conformation, labeled Conformation **2.**



Chair Conformations and Energy

- **The two chair conformations of cyclohexane are different, so they are not equally stable.**



Chair Conformations and Energy

- The two chair conformations of cyclohexane are different, so they are not equally stable.
- Larger axial substituents create destabilizing (and thus unfavorable) 1,3-diaxial interactions.
- In methylcyclohexane, each unfavorable H,CH_3 interaction destabilizes the conformation by 0.9 kcal/mol, so Conformation 2 is 1.8 kcal/mol less stable than Conformation 1.

The larger CH_3 group is equatorial.

Conformation 1

more stable
95%

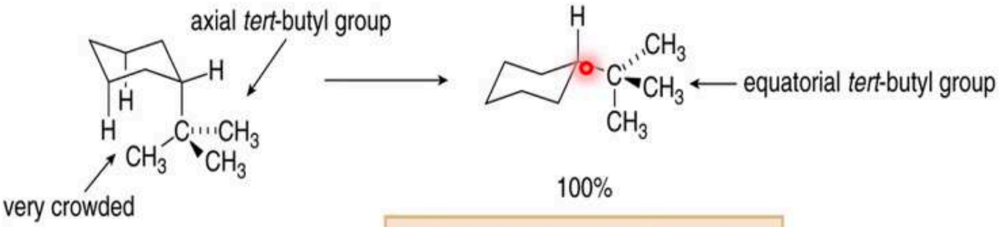
Conformation 2

5%

Preference of Equatorial Position in Substituted Cyclohexanes

- The larger the substituent on the six-membered ring, the higher the percentage of the equatorial conformation at equilibrium.
- With a very large substituent like *tert*-butyl [$(CH_3)_3C$-], essentially none of the conformation containing an axial *tert*-butyl group is present at room temperature.

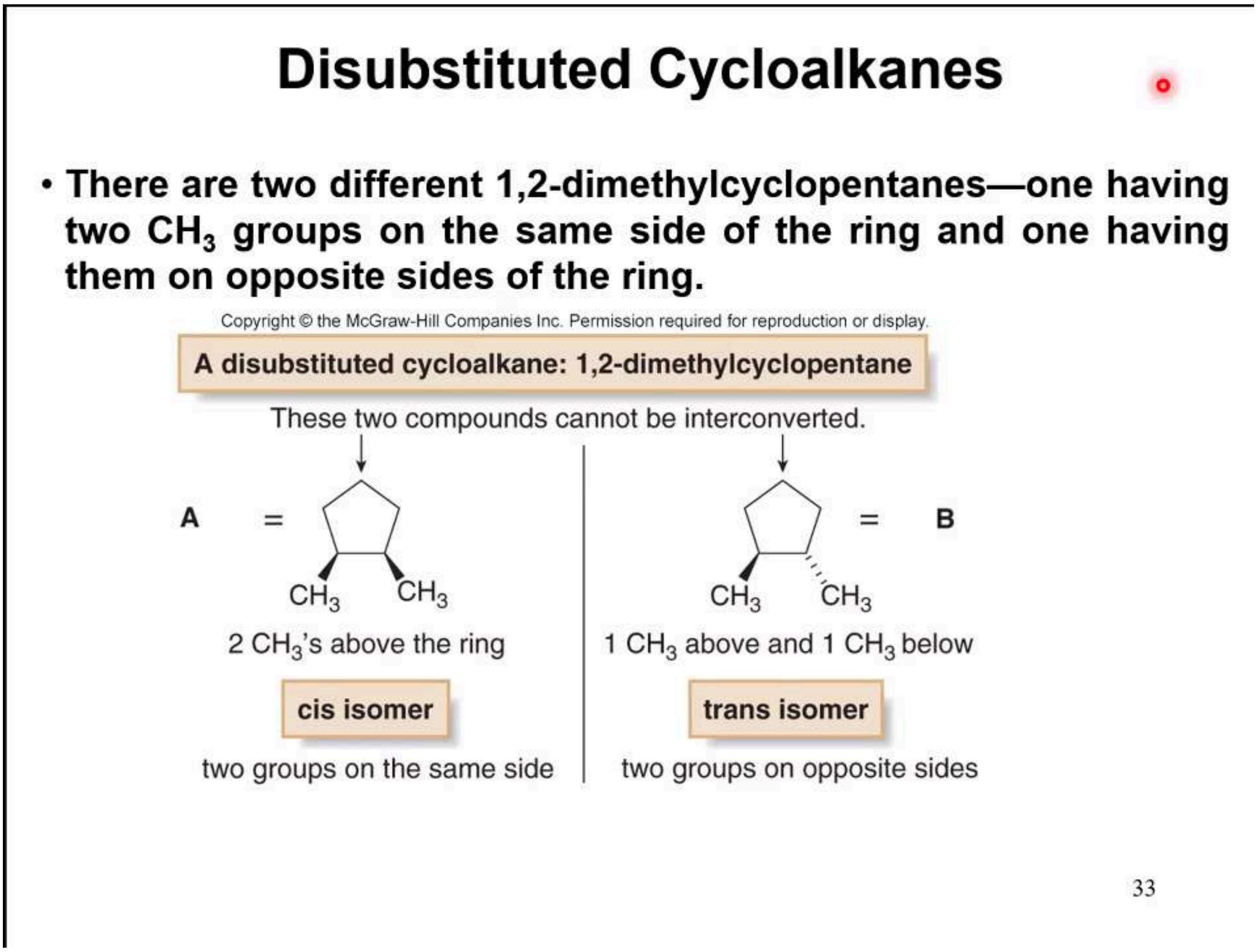
Figure 4.16



100%

highly destabilized

The large *tert*-butyl group anchors the cyclohexane ring in this conformation.



Disubstituted Cycloalkanes

- There are two different 1,2-dimethylcyclopentanes—one having two CH_3 groups on the same side of the ring and one having them on opposite sides of the ring.

A disubstituted cycloalkane: 1,2-dimethylcyclopentane

These two compounds cannot be interconverted.

2 CH_3's above the ring

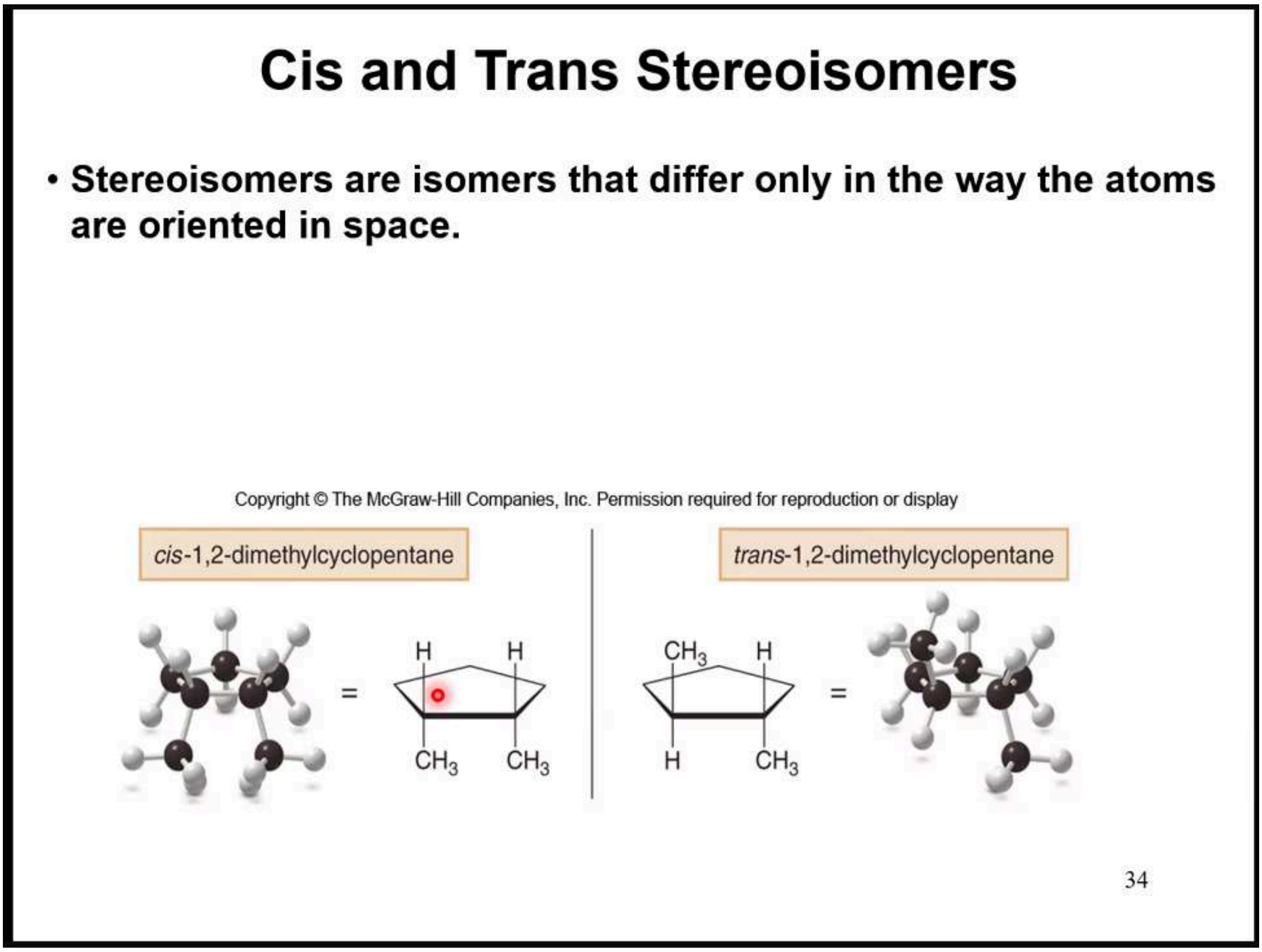
cis isomer

two groups on the same side

1 CH_3 above and 1 CH_3 below

trans isomer

two groups on opposite sides



Cis and Trans Stereoisomers

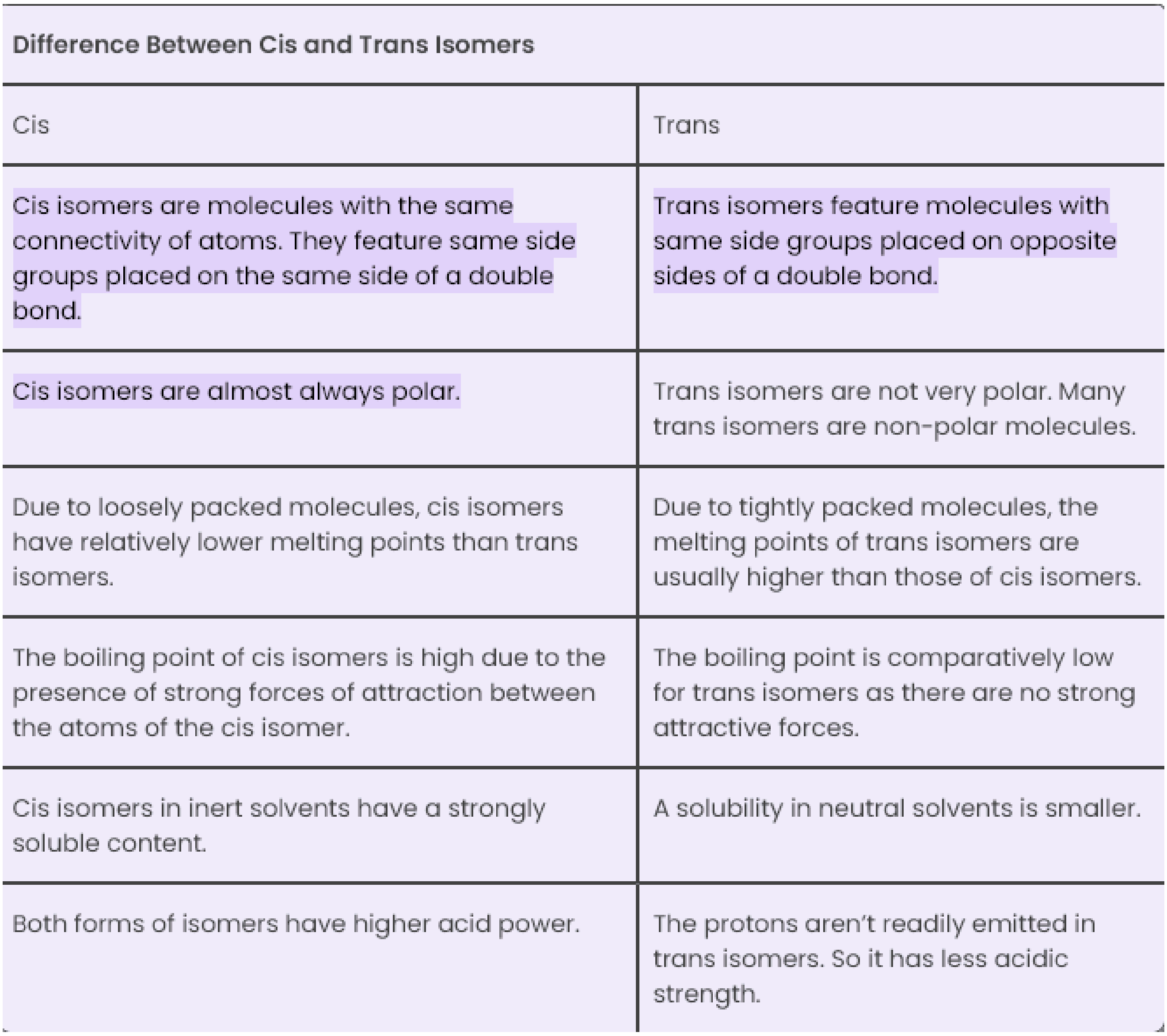
- Stereoisomers are isomers that differ only in the way the atoms are oriented in space.

cis-1,2-dimethylcyclopentane

trans-1,2-dimethylcyclopentane

Stereoisomers are isomers that differ only in the way the atoms are oriented in space.

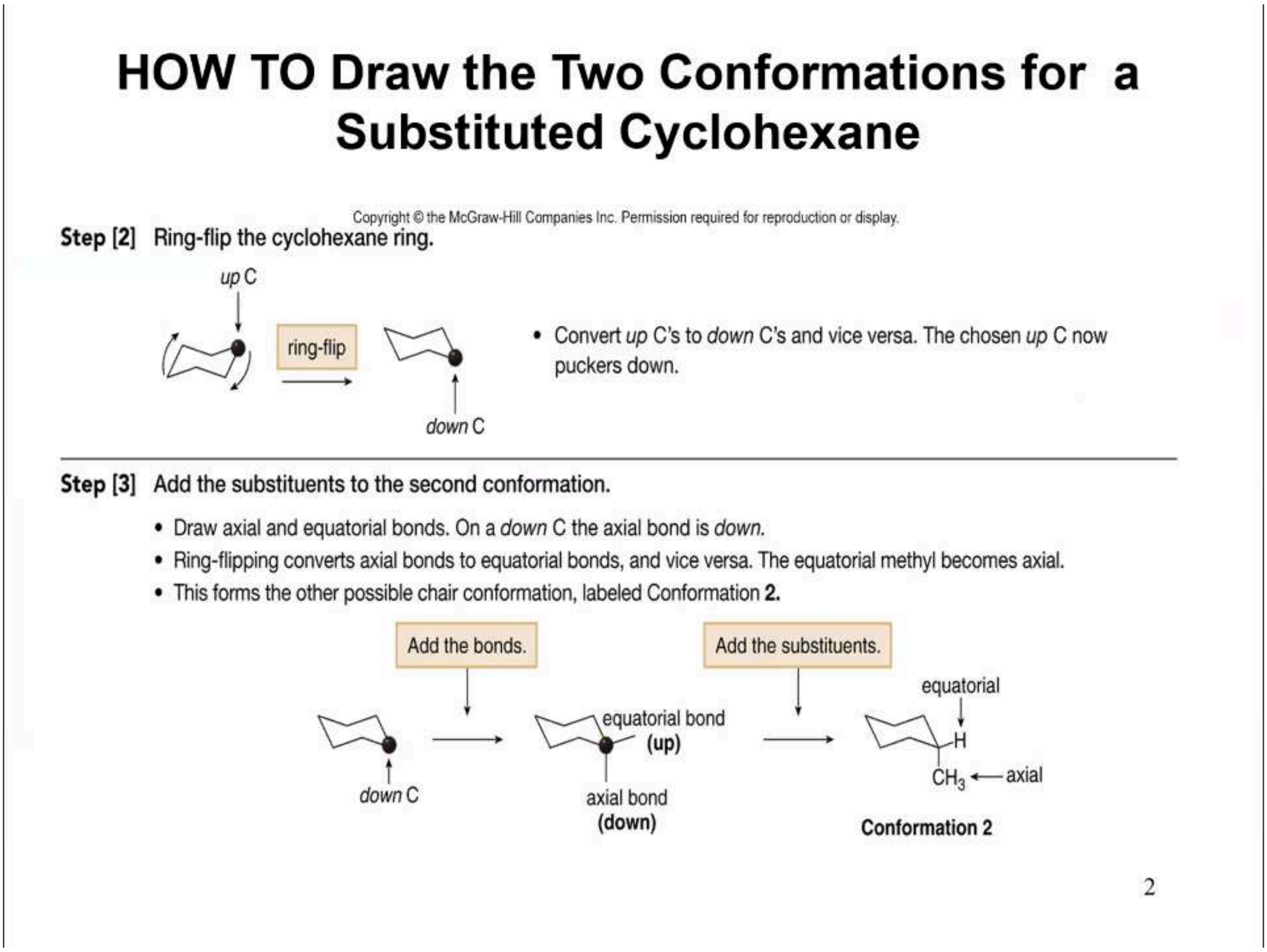
if both in down and up, cis
opposite - trans isomer



Difference Between Cis and Trans Isomers

Cis	Trans
Cis isomers are molecules with the same connectivity of atoms. They feature same side groups placed on the same side of a double bond.	Trans isomers feature molecules with same side groups placed on opposite sides of a double bond.
Cis isomers are almost always polar.	Trans isomers are not very polar. Many trans isomers are non-polar molecules.
Due to loosely packed molecules, cis isomers have relatively lower melting points than trans isomers.	Due to tightly packed molecules, the melting points of trans isomers are usually higher than those of cis isomers.
The boiling point of cis isomers is high due to the presence of strong forces of attraction between the atoms of the cis isomer.	The boiling point is comparatively low for trans isomers as there are no strong attractive forces.
Cis isomers in inert solvents have a strongly soluble content.	A solubility in neutral solvents is smaller.
Both forms of isomers have higher acid power.	The protons aren’t readily emitted in trans isomers. So it has less acidic strength.

Chapter 4: Alkanes



HOW TO Draw the Two Conformations for a Substituted Cyclohexane

Step [2] Ring-flip the cyclohexane ring.

- Convert *up* C's to *down* C's and vice versa. The chosen *up* C now puckers down.

Step [3] Add the substituents to the second conformation.

- Draw axial and equatorial bonds. On a *down* C the axial bond is *down.*
- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The equatorial methyl becomes axial.
- This forms the other possible chair conformation, labeled Conformation **2.**

Conformation 2

Up carbon - axial position is positioned higher than equatorial

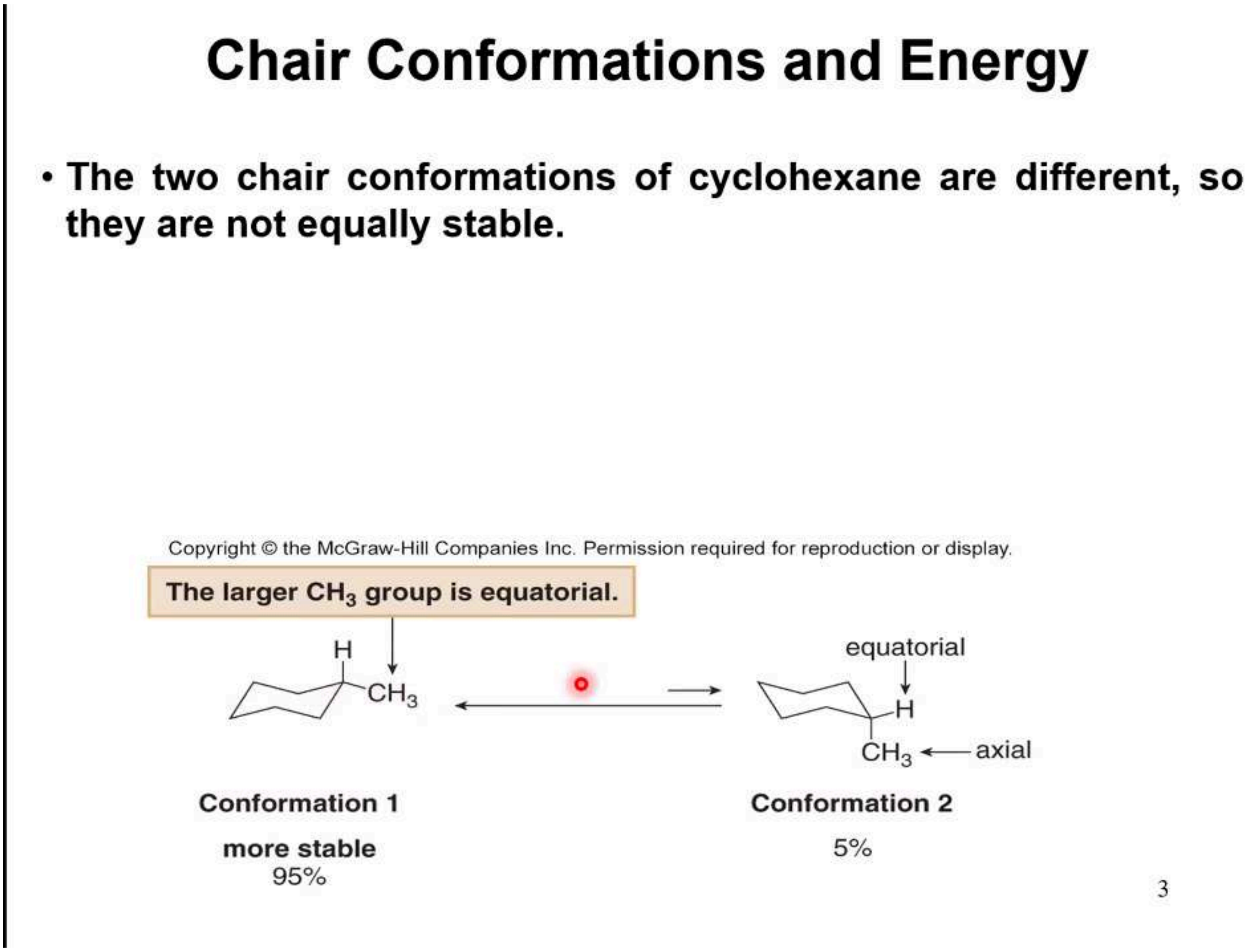
Down Carbon - axial position is positioned lower than equatorial

Ring flipping converts up to down and vice versa

Adding substituents to the second formation

Draw axial and equatorial bonds. On a down C the axial bond is down.

Ring flipping converts axial bonds to equatorial bonds and vice versa. Equatorial methyl becomes axial.



Chair Conformations and Energy

- **The two chair conformations of cyclohexane are different, so they are not equally stable.**

The larger CH_3 group is equatorial.

Conformation 1

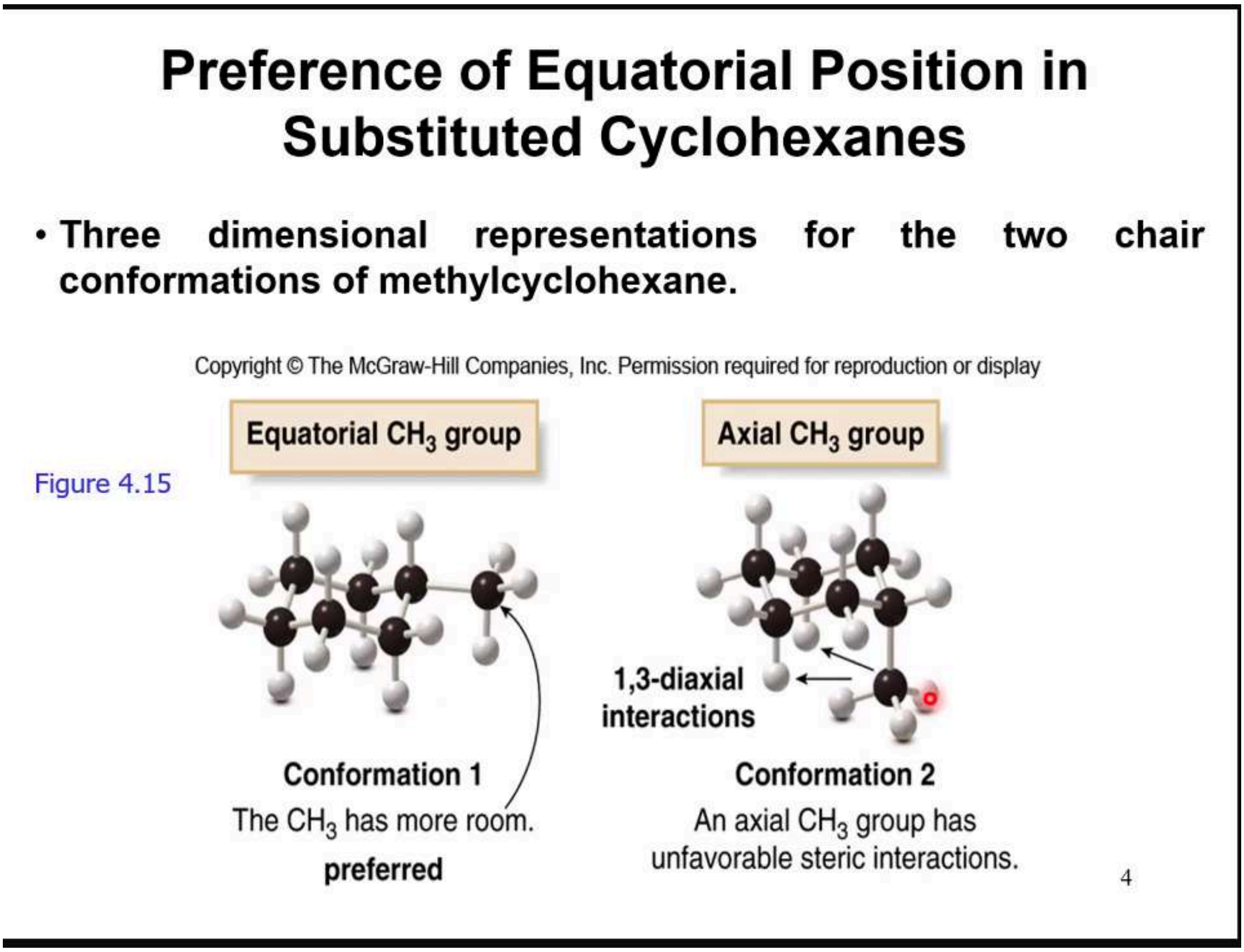
more stable
95%

Conformation 2

5%

two chair conformations of cyclohexane are different so they are not equally stable
larger CH3 group is equatorial so its more stable.

Larger axial susbtitents create destabilzing and unfavorable 13 diaxal



Preference of Equatorial Position in Substituted Cyclohexanes

- **Three dimensional representations for the two chair conformations of methylcyclohexane.**

Figure 4.15

Equatorial CH_3 group

Axial CH_3 group

1,3-diaxial interactions

Conformation 1

The CH_3 has more room.

preferred

Conformation 2

An axial CH_3 group has unfavorable steric interactions.

There are two different 1,2 -dimethylcyclopentanes - one having two ch3 groups on the same side of the ring and one having them on opposite sides of the ring

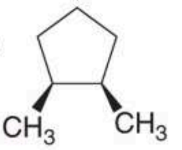
Disubstituted Cycloalkanes

- There are two different 1,2-dimethylcyclopentanes—one having two CH_3 groups on the same side of the ring and one having them on opposite sides of the ring.

A disubstituted cycloalkane: 1,2-dimethylcyclopentane

These two compounds cannot be interconverted.

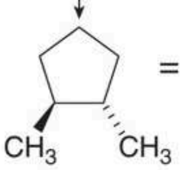
A =



2 CH_3's above the ring

cis isomer

two groups on the same side



= B

1 CH_3 above and 1 CH_3 below

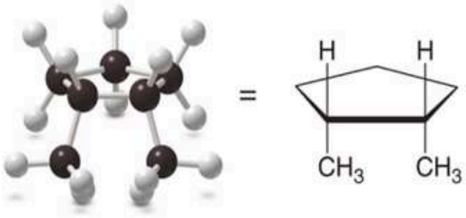
trans isomer

two groups on opposite sides

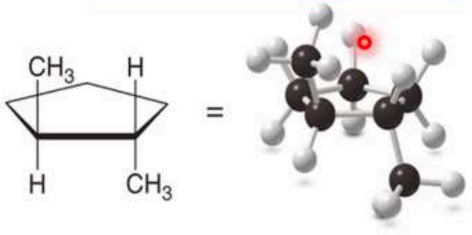
Cis and Trans Stereoisomers

- Stereoisomers are isomers that differ only in the way the atoms are oriented in space.

cis-1,2-dimethylcyclopentane



trans-1,2-dimethylcyclopentane



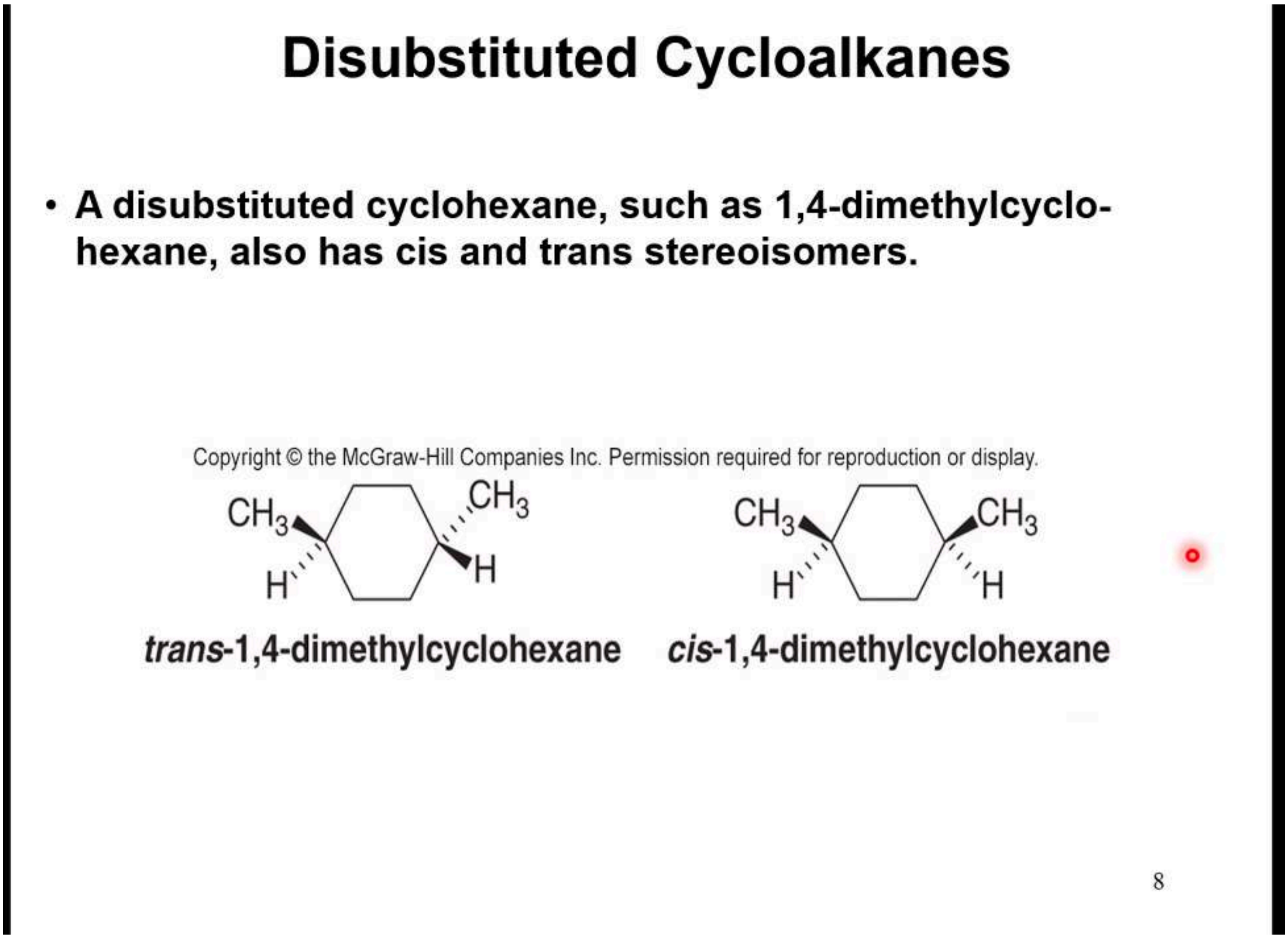
cis-1,2-dimethylcyclopentane

Stereoisomers- isomers that differ only in the way the atoms are oriented in space.

add cis- or trans- then iupac name

cis - two on same side

trans - two on opposite side



Disubstituted Cycloalkanes

- **A disubstituted cyclohexane, such as 1,4-dimethylcyclohexane, also has cis and trans stereoisomers.**

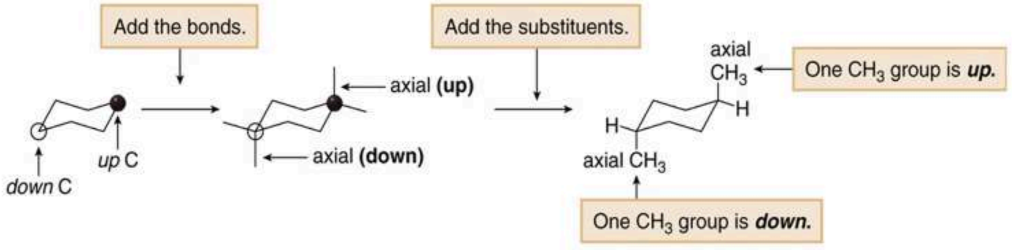
***trans*-1,4-dimethylcyclohexane** ***cis*-1,4-dimethylcyclohexane**

Drawing Disubstituted Cyclohexanes

HOW TO Draw Two Conformations for a Disubstituted Cyclohexane

Step [1] Draw one chair form and add the substituents.

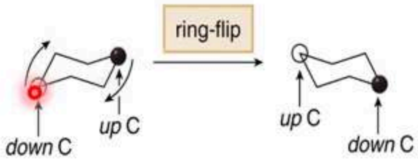
- For *trans*-1,4-dimethylcyclohexane, arbitrarily pick two C's located 1,4- to each other, classify them as *up* or *down* C's, and draw in the substituents.
- The trans isomer must have one group *above* the ring (on an *up* bond) and one group *below* the ring (on a *down* bond). The substituents can be either axial or equatorial, as long as one is up and one is down. The easiest trans isomer to visualize has two axial CH_3 groups. This arrangement is said to be **diaxial.**
- This forms one of the two possible chair conformations, labeled Conformation **1.**



Conformation 1

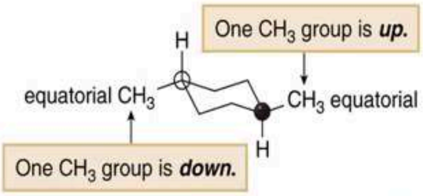
Drawing the Second Conformation of Cyclohexanes

Step [2] Ring-flip the cyclohexane ring.



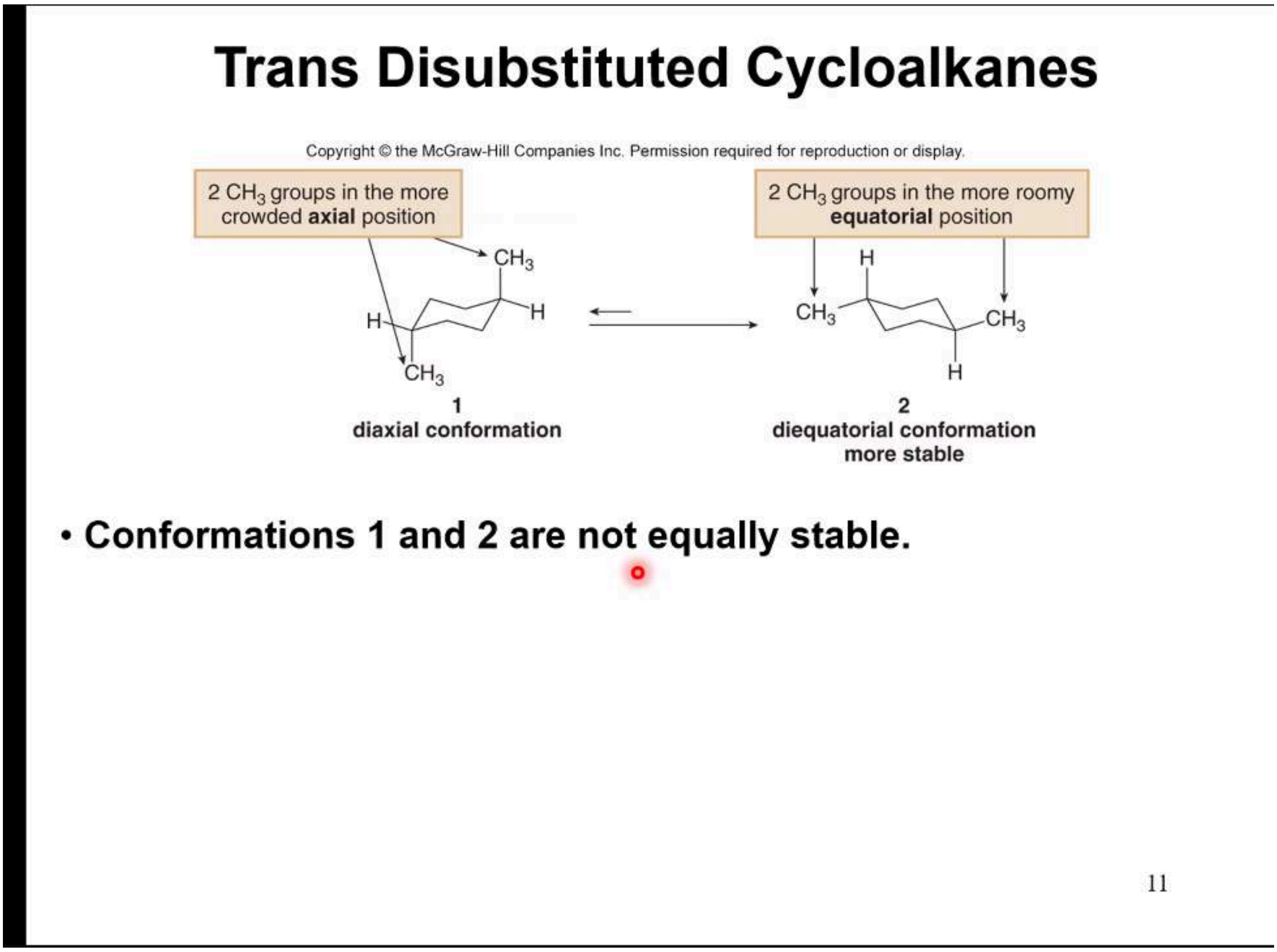
- The *up* C flips down, and the *down* C flips up.

Step [3] Add the substituents to the second conformation.



Conformation 2

- Ring-flipping converts axial bonds to equatorial bonds, and vice versa. The diaxial CH_3 groups become diequatorial. This trans conformation is less obvious to visualize. It is still trans, because one CH_3 group is above the ring (on an *up* bond), and one is below (on a *down* bond).



Trans Disubstituted Cycloalkanes

2 CH_3 groups in the more crowded **axial** position

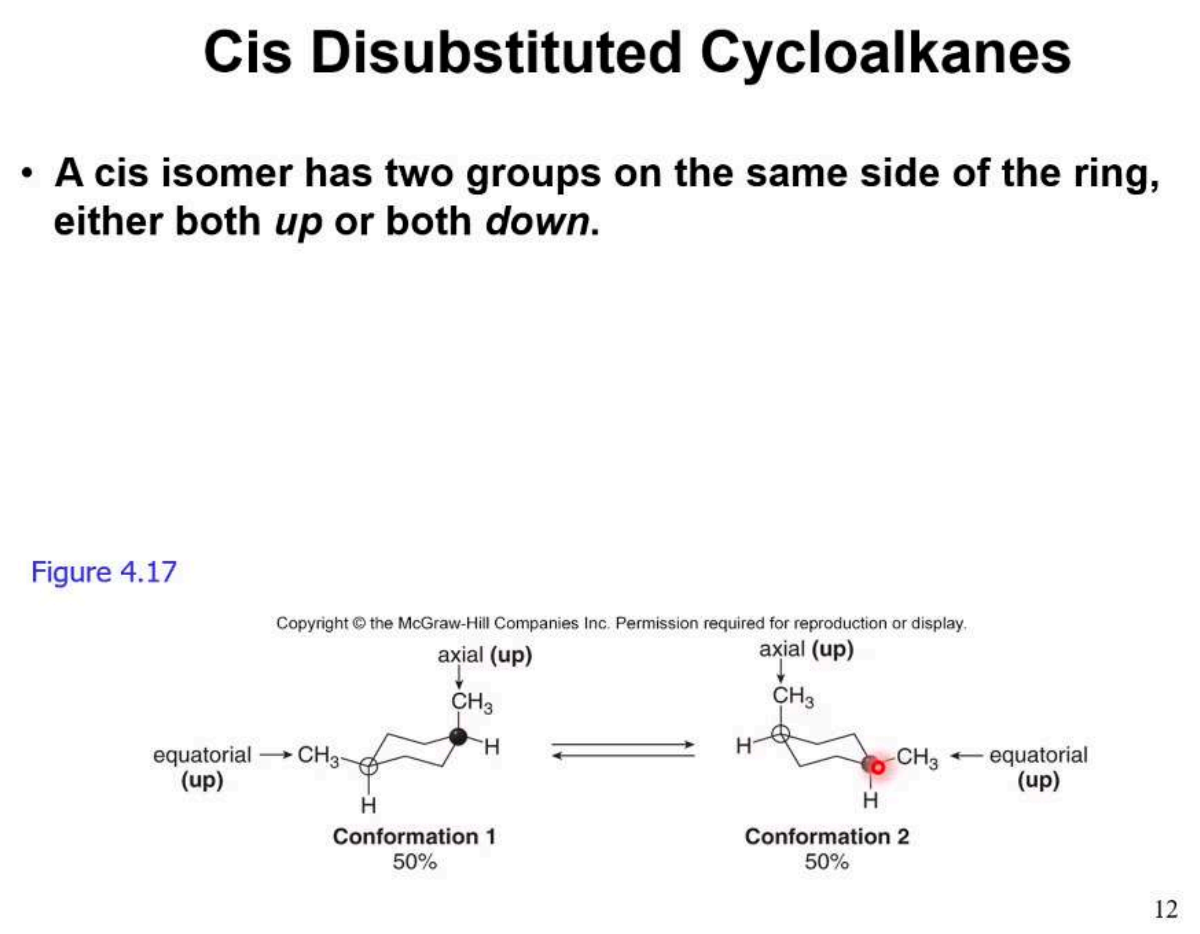
2 CH_3 groups in the more roomy **equatorial** position

1
diaxial conformation

2
diequatorial conformation
more stable

- **Conformations 1 and 2 are not equally stable.**

blah blah mas spread out equatorial more stable than axial
di equatorial, one slightly down CH3 one slightly up CH3



Cis Disubstituted Cycloalkanes

- **A cis isomer has two groups on the same side of the ring, either both *up* or both *down*.**

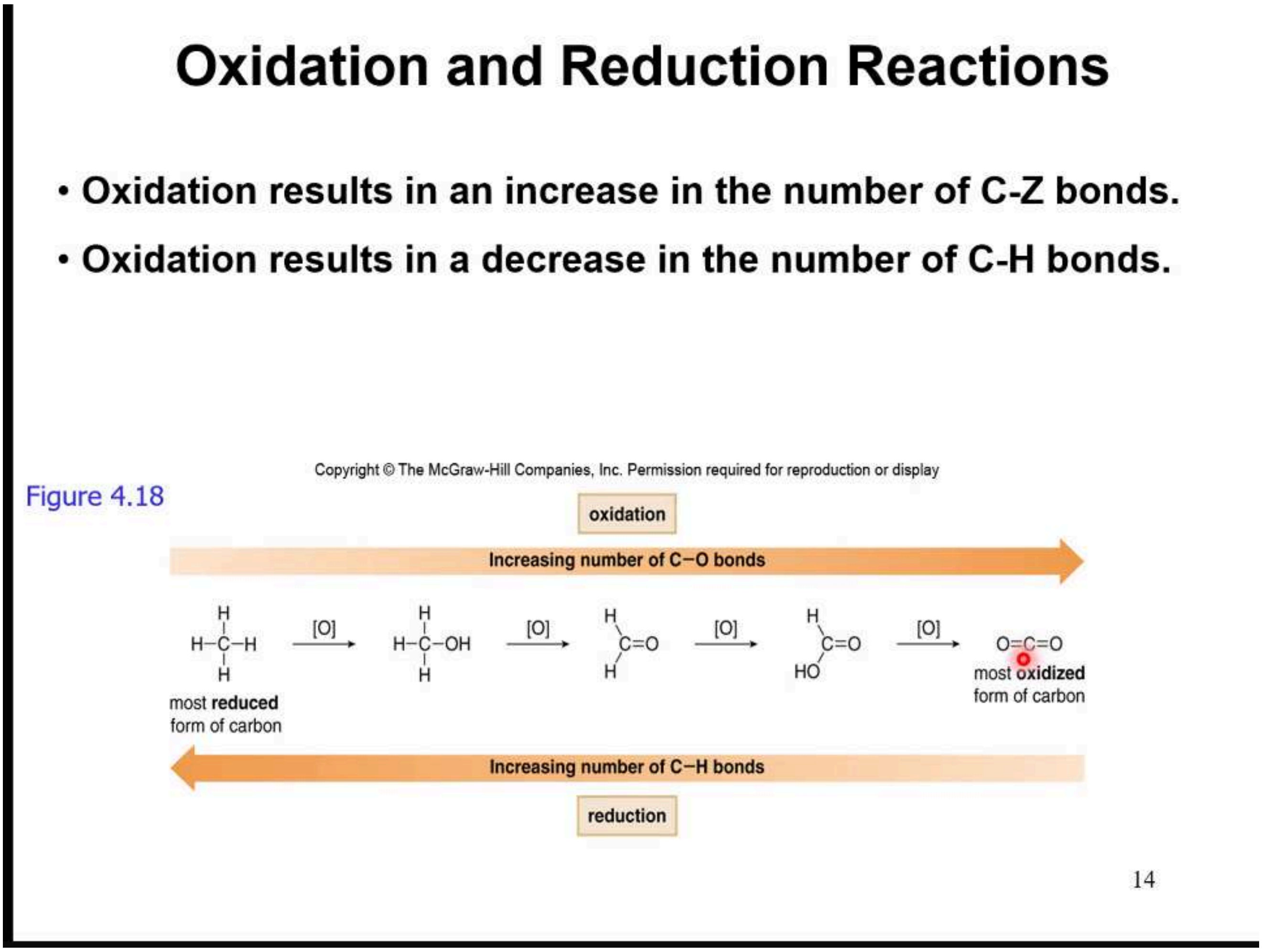
Figure 4.17

cis disubstituted cycloalkanes - equal equatorial and axial, equal occurence.

Oxidation and Reduction Reactions

Oxidation results in an increase in the number of C-Z bonds.
Z - heteroatom
oxidation - add O
alkane -> alcohol -> aldehyde -> carboxylic acid -> carbon dioxide
reduce - reduce O/ add H

alkane <- alcohol <- aldehyde <- carboxylic acid <- carbon dioxide



Oxidation and Reduction Reactions

- **Oxidation results in an increase in the number of C-Z bonds.**
- **Oxidation results in a decrease in the number of C-H bonds.**

Figure 4.18

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Stereochemistry

Recall that isomers are different compounds with the same molecular formula

two major classes of isomers are constitutional isomers and stereoisomers

1. constitutional/structural isomers have different iupac names, the same or different functional groups, different physical properties and different chemical properties
2. stereoisomers differ only in the way the atoms are oriented in space. They have identical IUPAC names except for a prefix like cis or trans. they always have the same functional group.
3. A particular three-dimensional arrangement is called a configuration. stereoisomers differ in configuration.

Stereochemistry

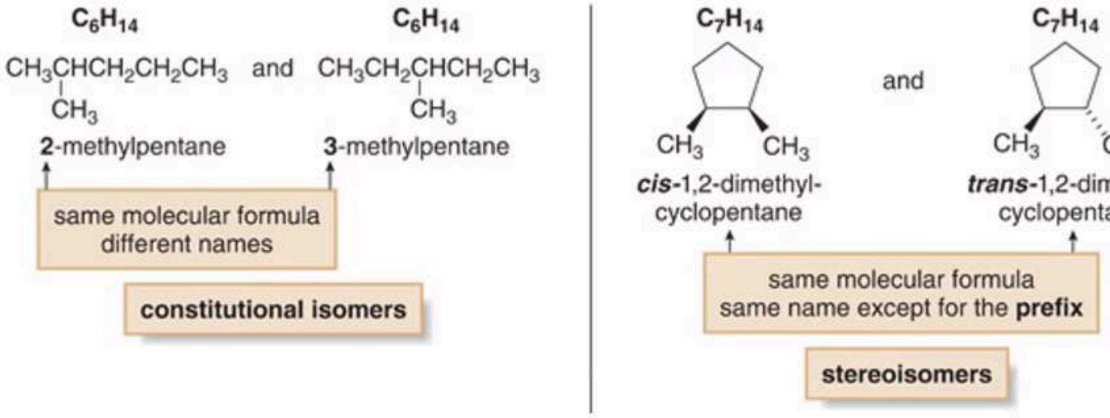
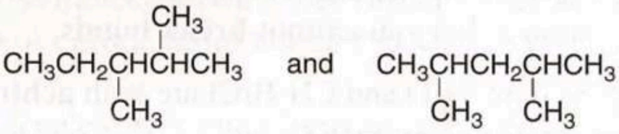


Figure 5.3 A comparison of constitutional isomers and stereoisomers

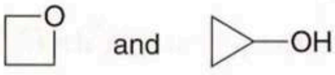
Classify each pair of compounds as constitutional isomers or stereoisomers.

a. 

$$CH_3CH_2\underset{CH_3}{CH}\overset{CH_3}{CH}CH_3 \quad \text{and} \quad CH_3\underset{CH_3}{CH}CH_2\underset{CH_3}{CH}CH_3$$

C C

c. 

b. 

C S

d. 

Chapter 7 Alkyl Halides Nucleophilic Substitution

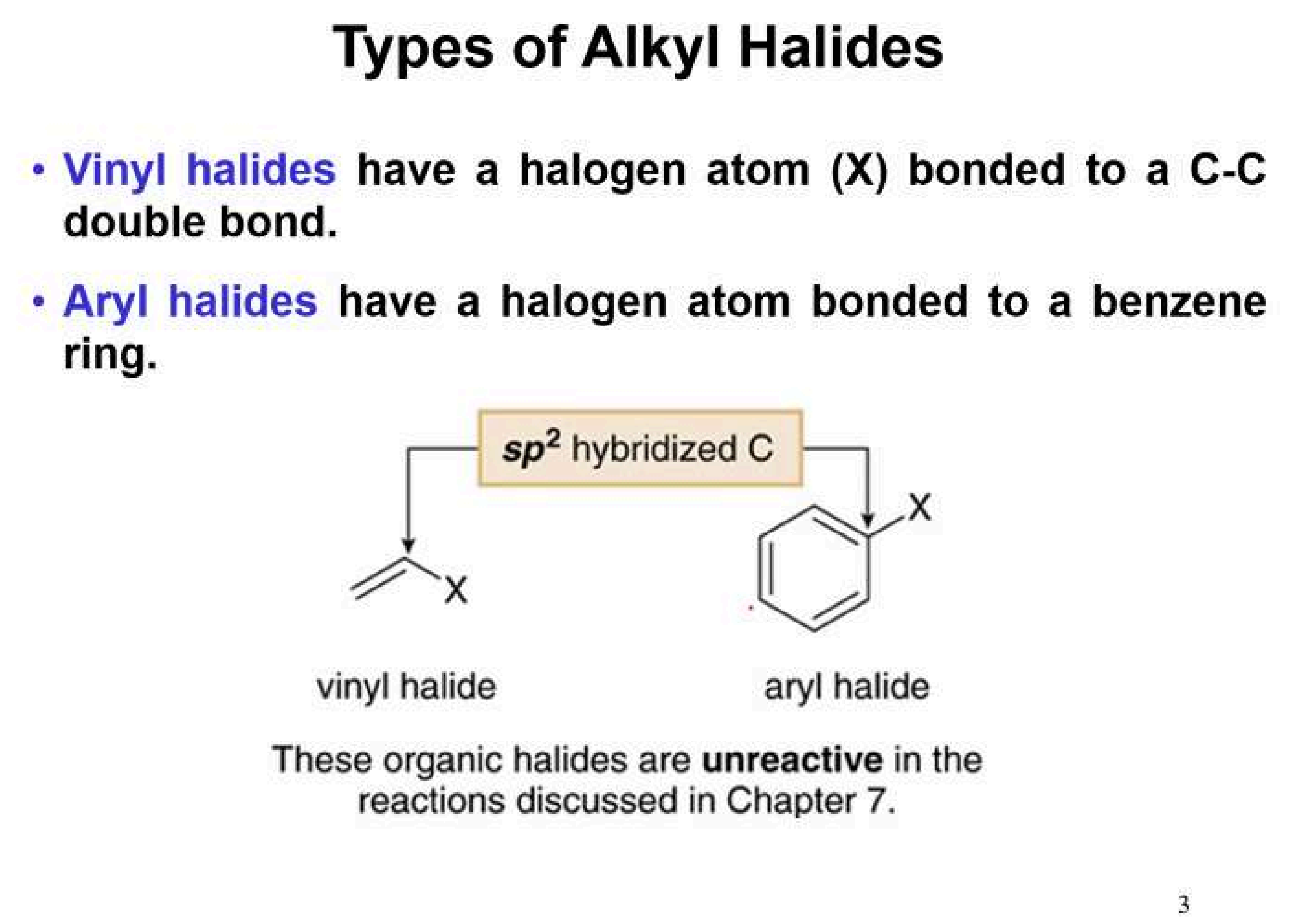
Alkyl halides

organic molecules containing a halogen atom bonded to a sp3 hybridized carbon atom.

The halogen in halides is denoted by X
classified as primary secondary tertiary depending on the number of carbons bonded to the carbon with the halogen atom.

vinyl halides have a halogen atom X bond to a C-C double bond sp2 hybridized

aryl halides have a halogen bonded to a benzene ring

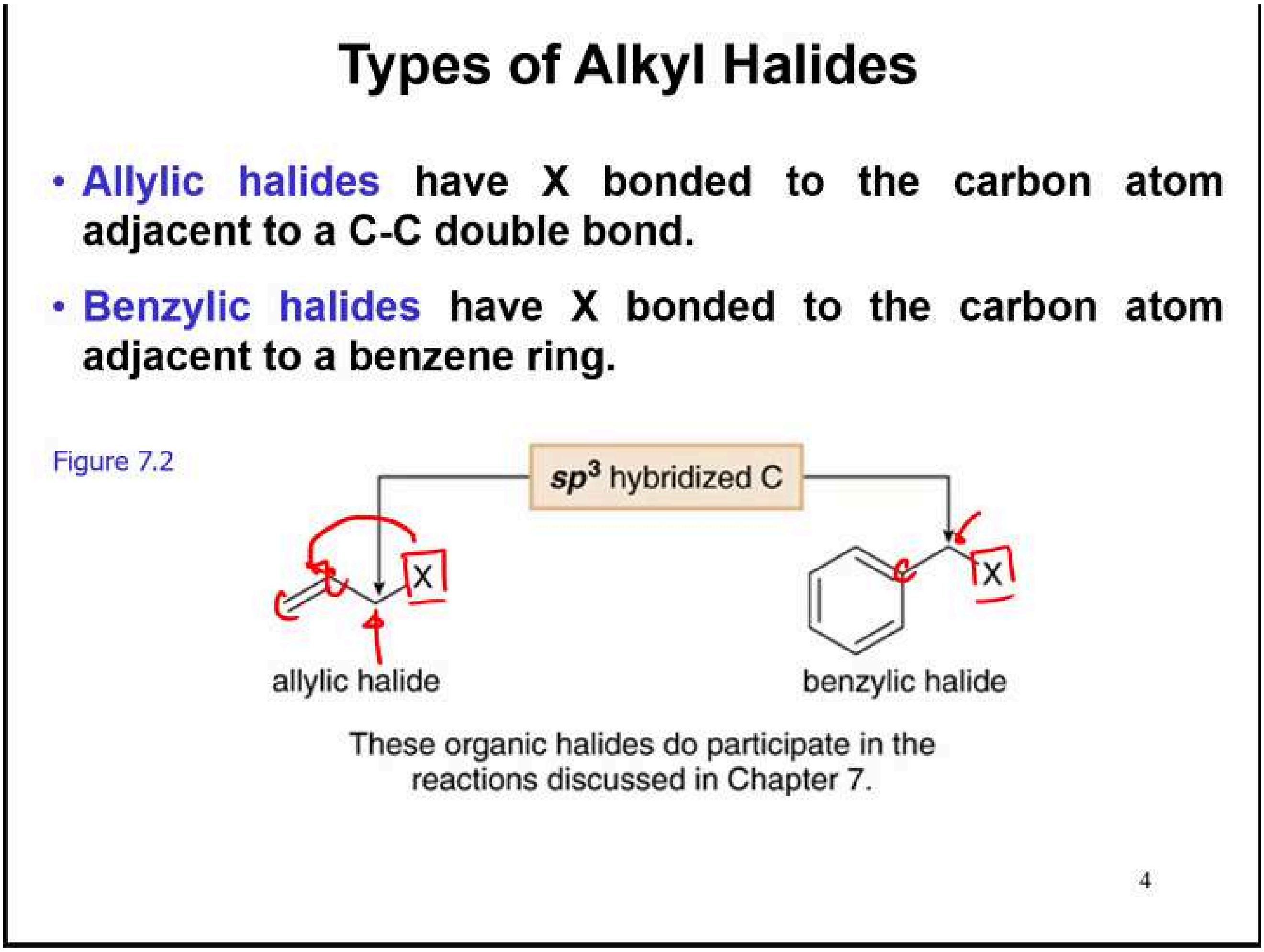


Types of Alkyl Halides

- **Vinyl halides** have a halogen atom (X) bonded to a C-C double bond.
- **Aryl halides** have a halogen atom bonded to a benzene ring.

These organic halides are **unreactive** in the reactions discussed in Chapter 7.

allylic halides have X bonded to the carbon atom adjacent to a C-C double bond benzylic halide have X bonded to a carbon bonded to a benzene ring



Types of Alkyl Halides

- **Allylic halides** have X bonded to the carbon atom adjacent to a C-C double bond.
- **Benzylic halides** have X bonded to the carbon atom adjacent to a benzene ring.

Figure 7.2

These organic halides do participate in the reactions discussed in Chapter 7.

nomenclature of alkyl halides

step 1. find the parent carbon chain thats bonded to the halogen (alkane)

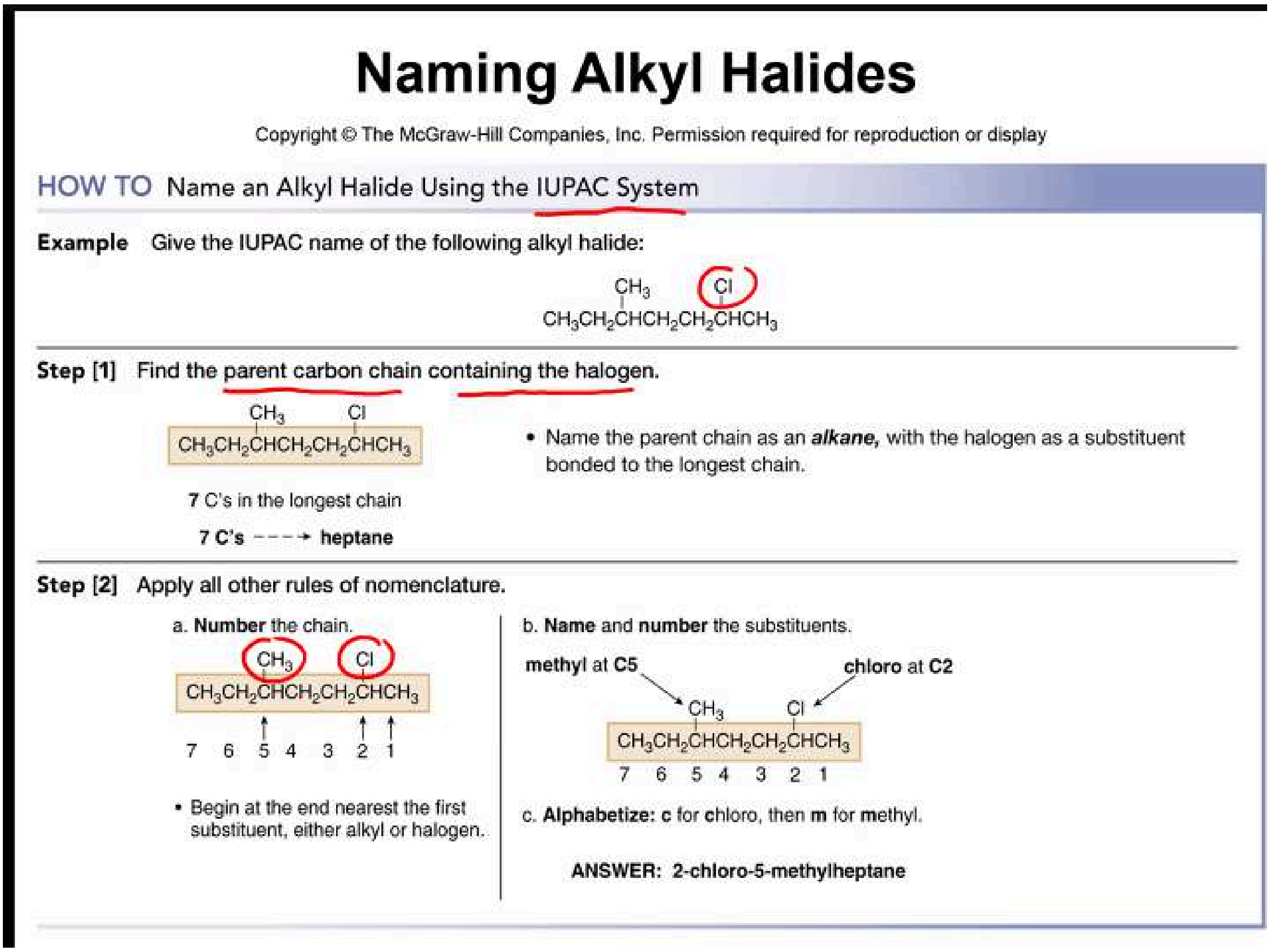
halogen serves as a substituent

all rules of nomenclature

a. number the chain

b. name and number the substituents

alphabetize



Naming Alkyl Halides

HOW TO Name an Alkyl Halide Using the IUPAC System

Example Give the IUPAC name of the following alkyl halide:

$CH_3CH_2CH(CH_3)CH_2CH_2CH(Cl)CH_3$

Step [1] Find the parent carbon chain containing the halogen.

$CH_3CH_2CH(CH_3)CH_2CH_2CH(Cl)CH_3$

7 C's in the longest chain

7 C's - - - → **heptane**

- Name the parent chain as an ***alkane,*** with the halogen as a substituent bonded to the longest chain.

Step [2] Apply all other rules of nomenclature.

a. **Number** the chain.

$CH_3CH_2CH(CH_3)CH_2CH_2CH(Cl)CH_3$

7 6 5 4 3 2 1

- Begin at the end nearest the first substituent, either alkyl or halogen.

b. **Name** and **number** the substituents.

methyl at **C5**

chloro at **C2**

$CH_3CH_2CH(CH_3)CH_2CH_2CH(Cl)CH_3$

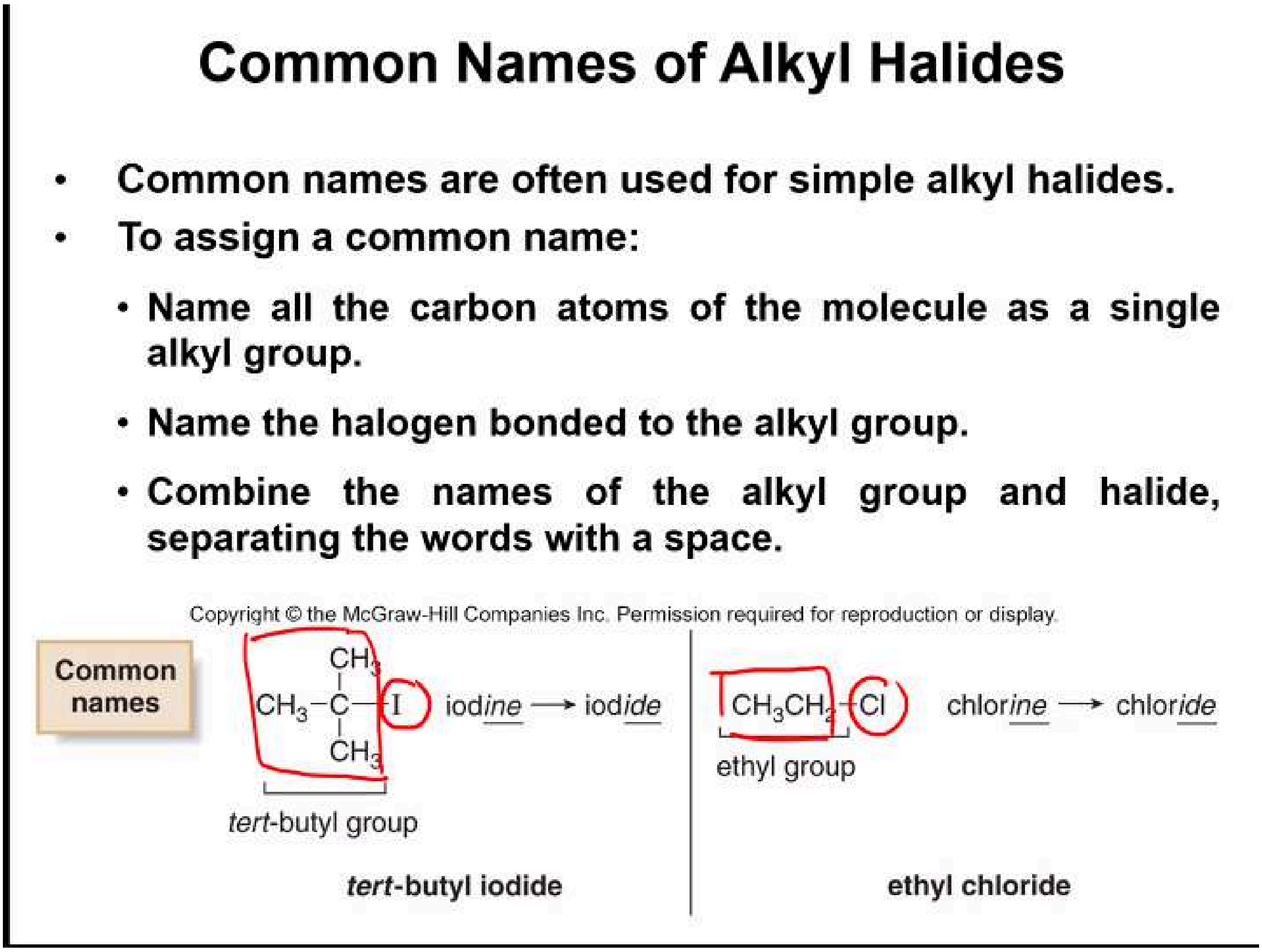
7 6 5 4 3 2 1

c. **Alphabetize: c** for **c**hloro, then **m** for **m**ethyl.

ANSWER: 2-chloro-5-methylheptane

common names are ofeten used for simple alkyl halides
to assign a common name

name all the carbon atoms of the molecule as a single akyl group
then



Common Names of Alkyl Halides

- **Common names are often used for simple alkyl halides.**
- **To assign a common name:**
  - **Name all the carbon atoms of the molecule as a single alkyl group.**
  - **Name the halogen bonded to the alkyl group.**
  - **Combine the names of the alkyl group and halide, separating the words with a space.**

Common names

***tert*-butyl iodide**

ethyl chloride

halogen - halide
iodine - iodide
chlorine - chloride

alkyl halides are weakly polar molecules
they exhibit dipole dipole interactions beacuse of their polar C-X bond.

since the rest of the molecule contains only C-C and C-H bonds, they are incapable of intermolecular hydrogen bonding

dipole dipole, van der waals

alkyl halides have higher bps and mps than alkanes having the same number of carbons (alkyl halide has more imfs)

bps and mps increasse as size of R increase (larger surface area)

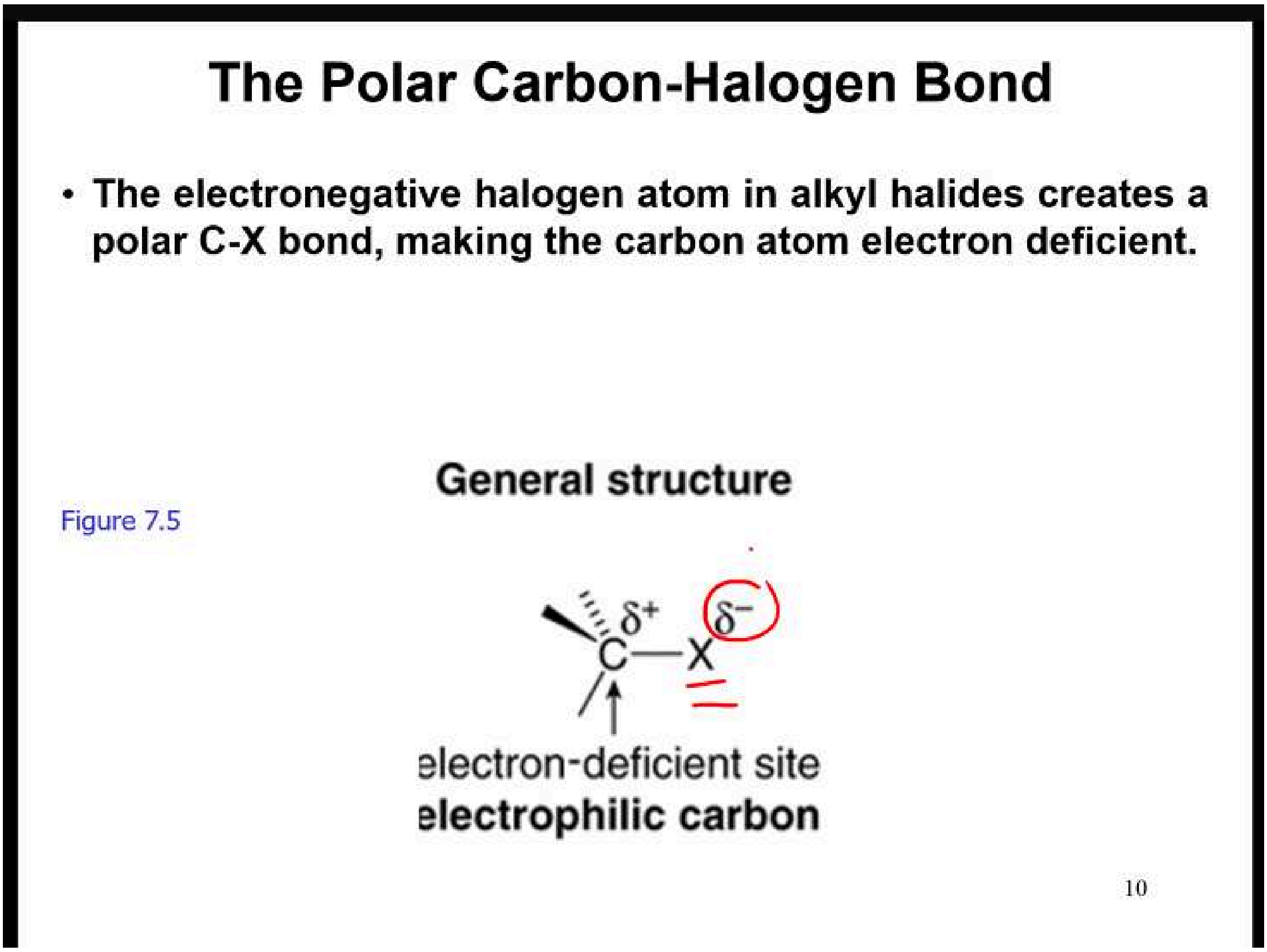
bps and mps increase as the size of X incerase (more polarizable halogen higher mp and bp)

RX is soluble in organic solvents

RX is insoluble in water

polar carbon halogen bond

the electronegative halogen atom in alkyl halides creates a polar C-X bond, making the carbon atom electron deficient.



The Polar Carbon-Halogen Bond

- **The electronegative halogen atom in alkyl halides creates a polar C-X bond, making the carbon atom electron deficient.**

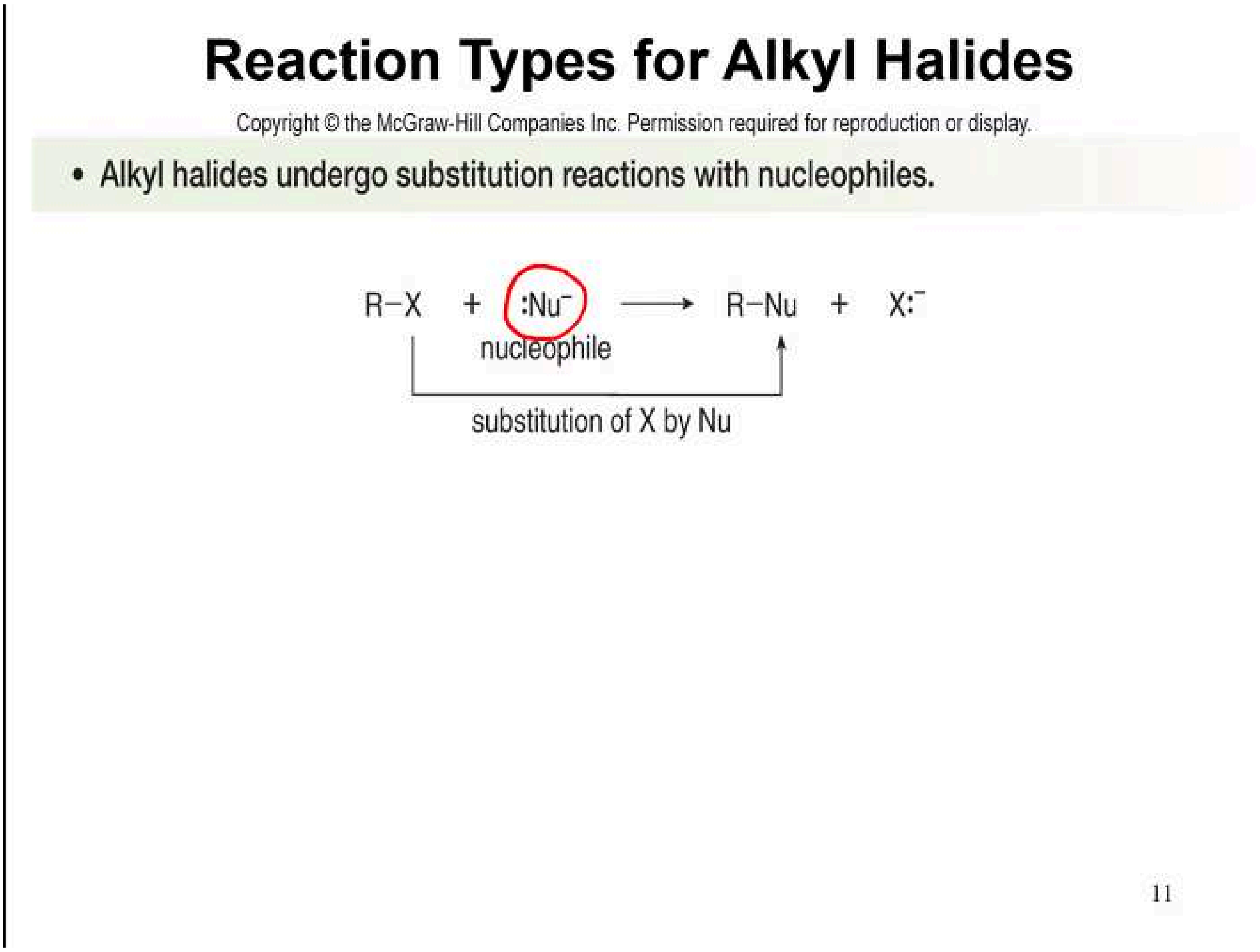
General structure

Figure 7.5

electron-deficient site

electrophilic carbon

alkyl halides undergo substitution reactions with nucleophiles



Reaction Types for Alkyl Halides

- Alkyl halides undergo substitution reactions with nucleophiles.

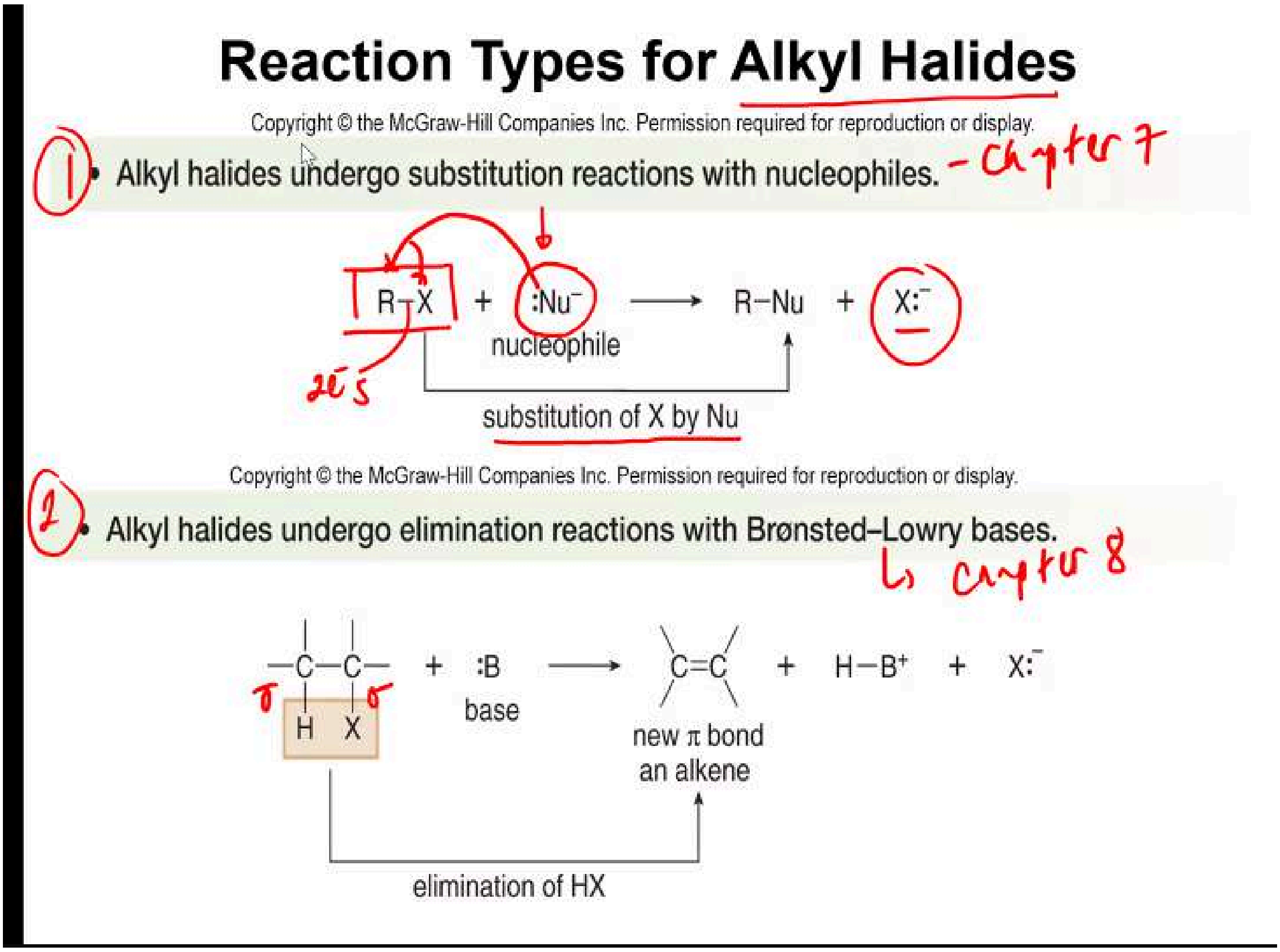
$$R{-}X \;+\; :Nu^- \longrightarrow R{-}Nu \;+\; X:^-$$

nucleophile

substitution of X by Nu

nucleophile targets electrophilic center (R)
so X can be substituted by nucleophile
when substituted, halogen becomes a negative nucleophile

alkyl halides undergo elimination reactions with bronsted lowry bases



Reaction Types for Alkyl Halides

① • Alkyl halides undergo substitution reactions with nucleophiles. - chapter 7

$$R{-}X + {:}Nu^- \longrightarrow R{-}Nu + X{:}^-$$

② • Alkyl halides undergo elimination reactions with Brønsted–Lowry bases.
↳ chapter 8

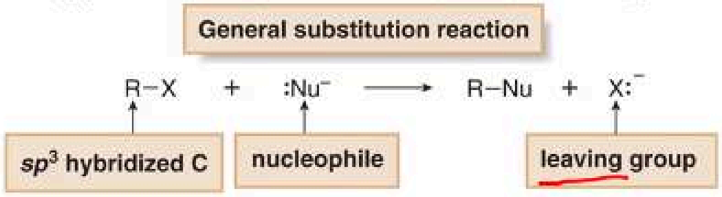
substitution reactions

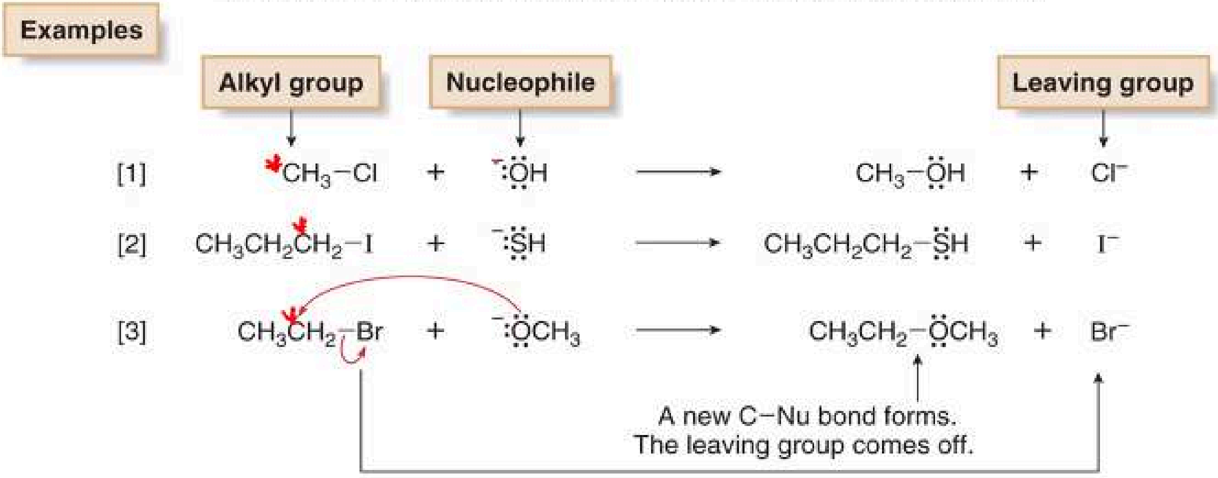
three components are necessary in any substitution reaction

sp3 hybridized C -X + Nu- = R-Nu + X-

Substitution Reactions

- **Three components are necessary in any substitution reaction.**

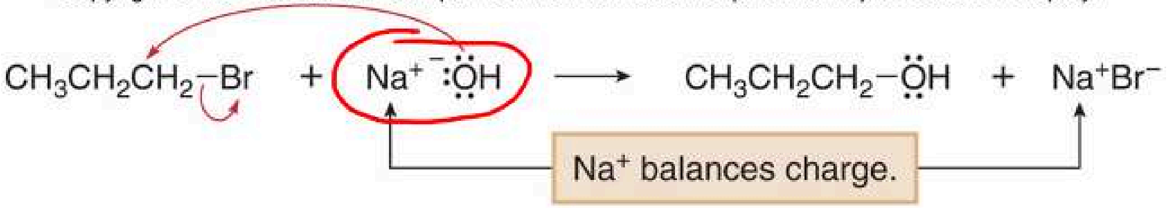




nucleophiles are lewis bases that can be negatively chrged or neutral
negatively charged nucleophiles like HO- and HS- are used as salts with Li, Na or K to balance the chrge

Nucleophiles in Substitution Reactions

- Nucleophiles are Lewis bases that can be negatively charged or neutral.
- Negatively charged nucleophiles like HO^- and HS^- are used as salts with Li^+, Na^+, or K^+ counterions to balance the charge.

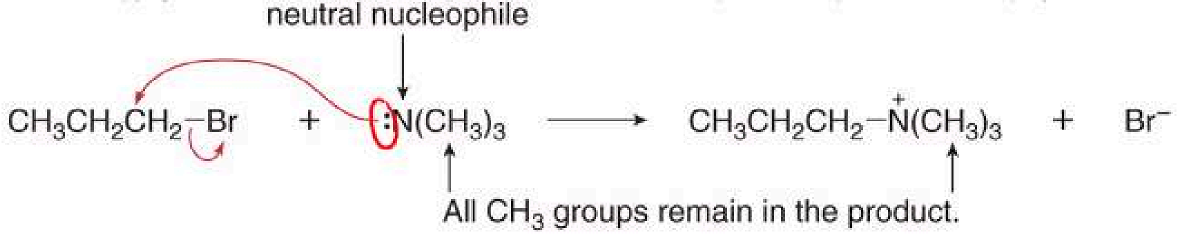


neutral nucleophile

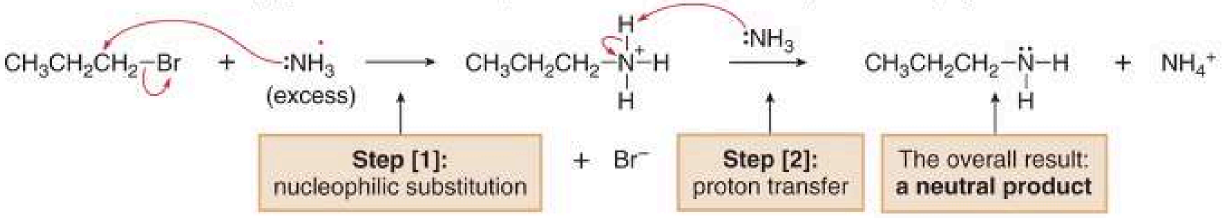
when a neutral nucleophile is used the substitution bears a positve charge

Neutral Nucleophiles

- When a neutral nucleophile is used, the substitution product bears a positive charge.



Drawing Products of Nucleophilic Substitution Reactions

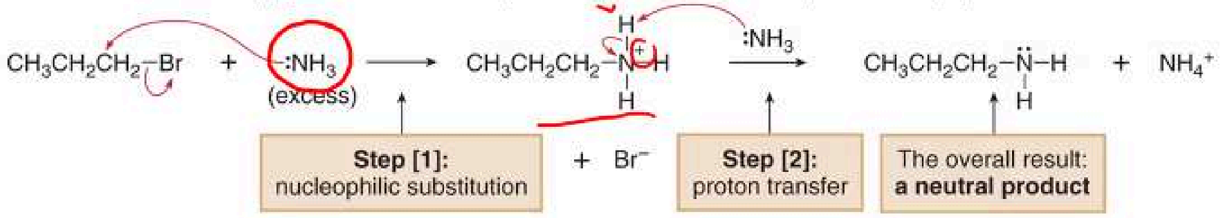


Step [1]: nucleophilic substitution

Step [2]: proton transfer

The overall result: **a neutral product**

Drawing Products of Nucleophilic Substitution Reactions



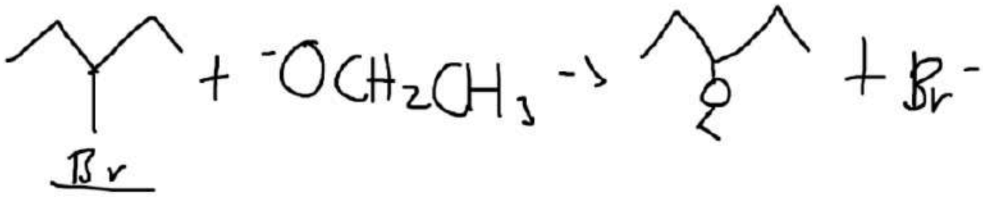
Step [1]: nucleophilic substitution

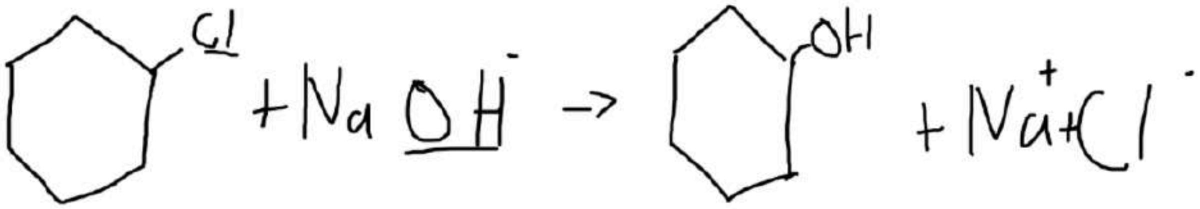
Step [2]: proton transfer

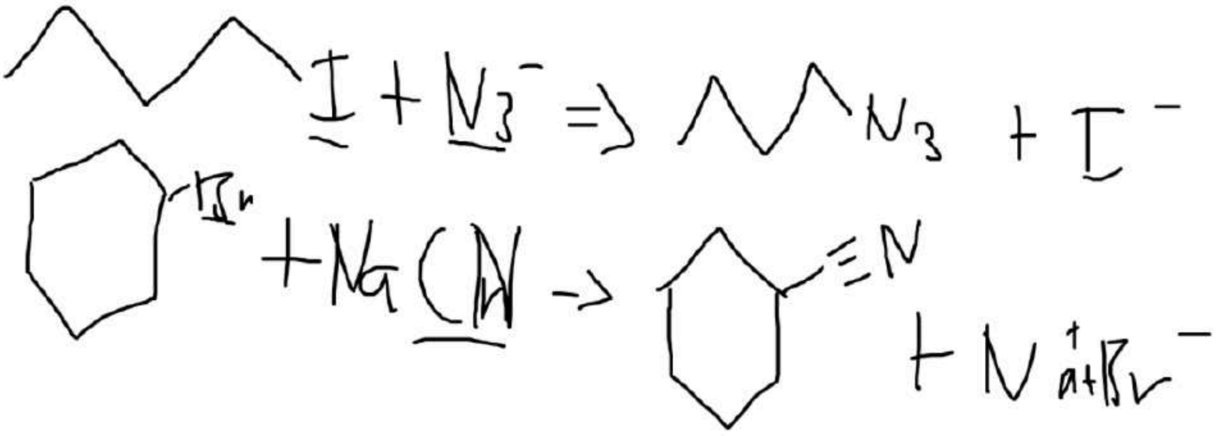
The overall result: **a neutral product**

- **The overall effect of any nucleophilic substitution is the replacement of the leaving group by the nucleophile.**
- **To draw any nucleophilic substitution product:**
  - **Find the *sp*^{3} hybridized carbon with the leaving group.**
  - **Identify the nucleophile, the species with a lone pair or π bond.**

for org reaction excess reagent to complete reaction







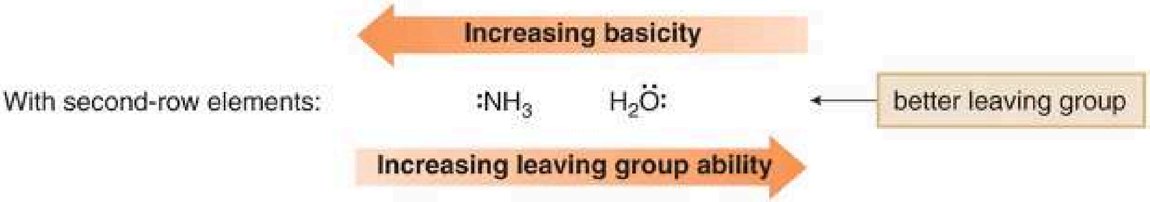
In a nucleophilic substitution reaction of R-X, the C-X bond is heterolytically cleaved, and the leaving group departs with the electron pair in that bond forming X-
the stable the leaving group X-, the better able it is to accept an electron pair

H2O is a better leaving group
weaker base better leaving group

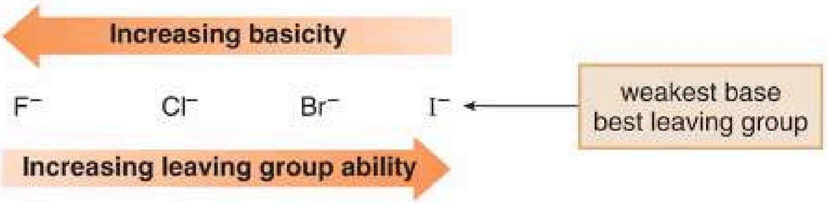
Trends in Leaving Group Ability

- **The weaker the base, the better the leaving group.**

- Left-to-right across a row of the periodic table, basicity *decreases* so leaving group ability *increases.*



- Down a column of the periodic table, basicity *decreases* so leaving group ability *increases.*



Poor Leaving Groups

- **Conjugate bases of weaker acids are poorer leaving groups.**

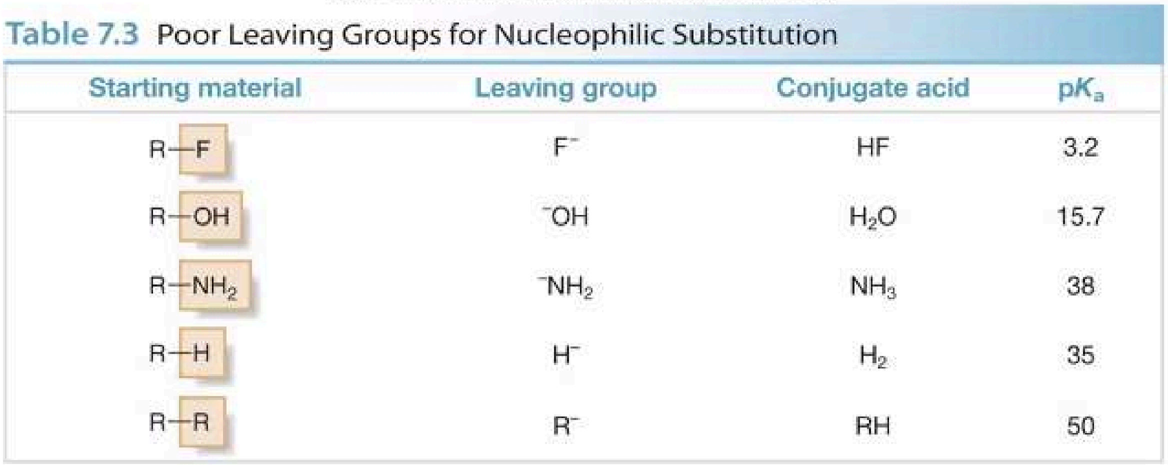


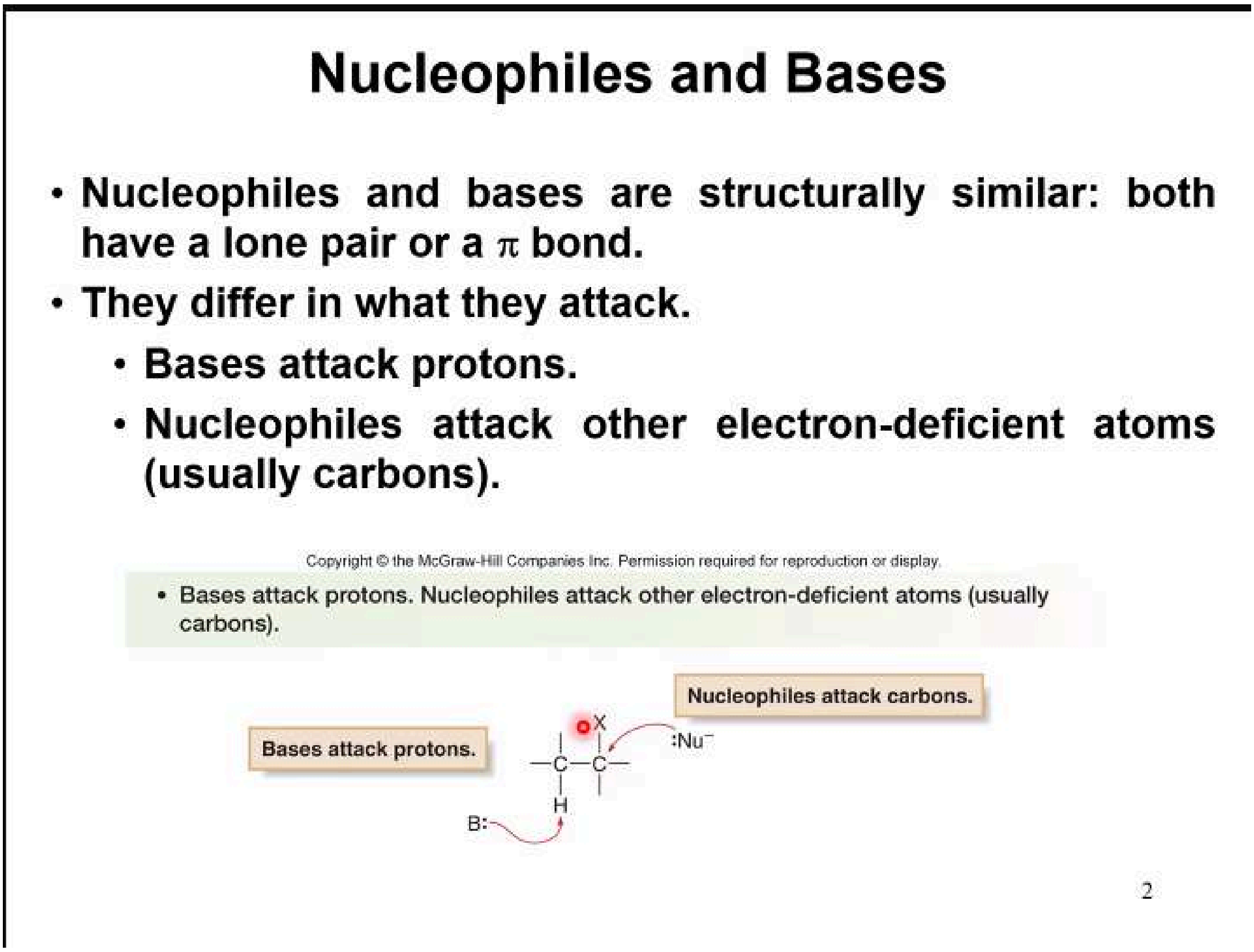
Table 7.3 Poor Leaving Groups for Nucleophilic Substitution

Starting material	Leaving group	Conjugate acid	pK_a
R—F	F^-	HF	3.2
R—OH	^-OH	H_2O	15.7
R—NH_2	$^-NH_2$	NH_3	38
R—H	H^-	H_2	35
R—R	R^-	RH	50

nucleophiles and bases are structurally similar; both have a lone pair or a pi bond

nucleophiles and bases are structurally similar; both have a lone pair or a pi bond

They differ in what they attack
bases attack protons
nucleophiles attack other electron deficient atoms (usually carbons)



Nucleophiles and Bases

- **Nucleophiles and bases are structurally similar: both have a lone pair or a π bond.**
- **They differ in what they attack.**
  - **Bases attack protons.**
  - **Nucleophiles attack other electron-deficient atoms (usually carbons).**

- Bases attack protons. Nucleophiles attack other electron-deficient atoms (usually carbons).

Bases attack protons.

Nucleophiles attack carbons.

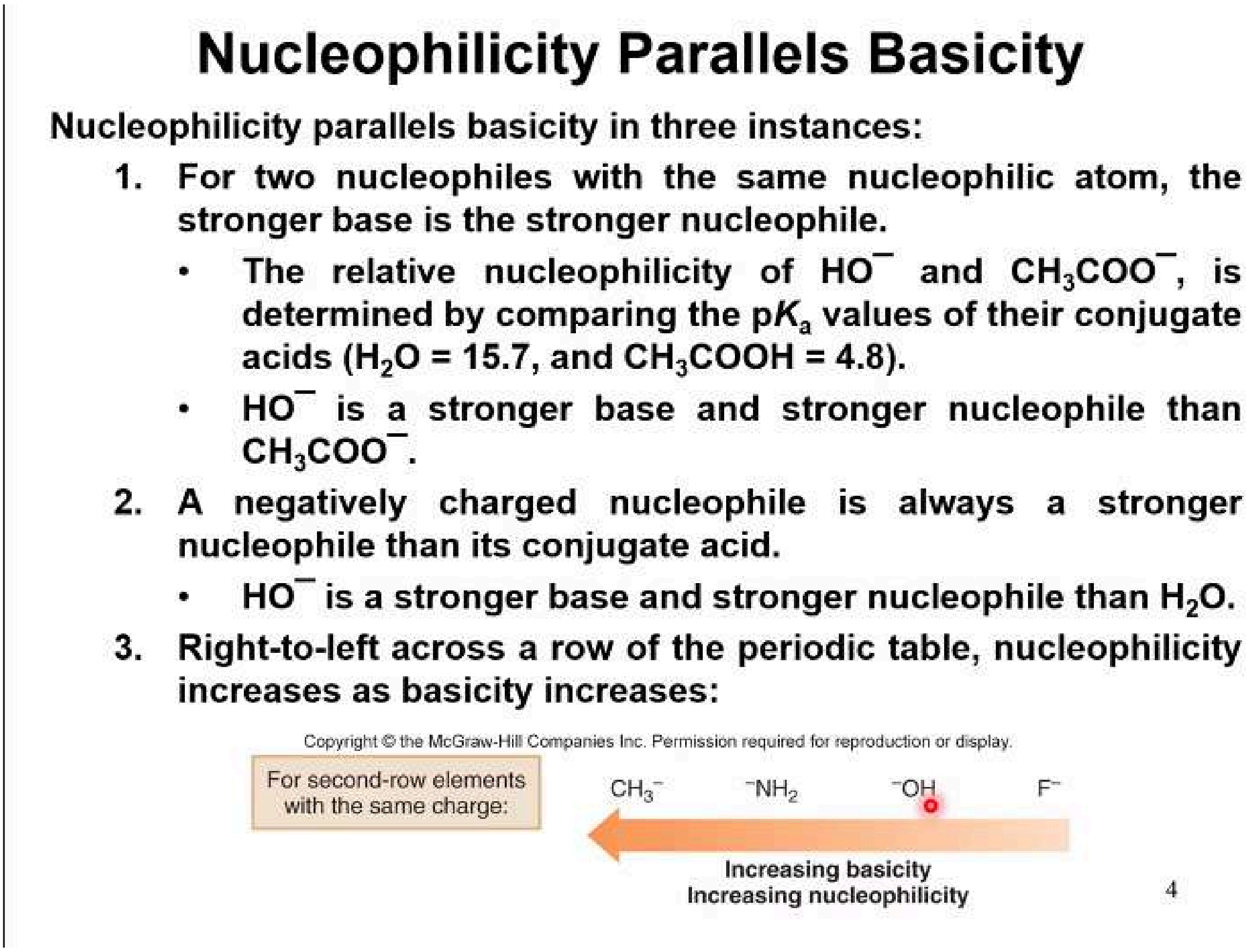
althoughly nucleophilicity and basicity are interelated
they are fundamentally different

nucleophilicity parallels basicity in three instances

for two nucleophiles with the same nucleophilic atom, the stronger base is the stronger nucleophile
relative nucleo of HO- and CH3COO- is determined by comparing the pKa values of conj acid
H2O = 15.7, CH3COOH = 4.8
H2O is weaker acid, so HO is stronger base
stronger the acid, the weaker the conjugate base.

a negatively charged nucleophile is always a stronger nucleophile than its conjugate acid
HO- is stronger base and nucleophile than H2O

RIGHT TO LEFT ACROSS A ROW OF PERIODIC TABLE, NUCLEOPHILICITY INCREASES AS BASICITY INCREASES



Nucleophilicity Parallels Basicity

Nucleophilicity parallels basicity in three instances:

1. **For two nucleophiles with the same nucleophilic atom, the stronger base is the stronger nucleophile.**
   - **The relative nucleophilicity of HO^- and CH_3COO^-, is determined by comparing the pK_a values of their conjugate acids (H_2O = 15.7, and CH_3COOH = 4.8).**
   - **HO^- is a stronger base and stronger nucleophile than CH_3COO^-.**
2. **A negatively charged nucleophile is always a stronger nucleophile than its conjugate acid.**
   - **HO^- is a stronger base and stronger nucleophile than H_2O.**
3. **Right-to-left across a row of the periodic table, nucleophilicity increases as basicity increases:**

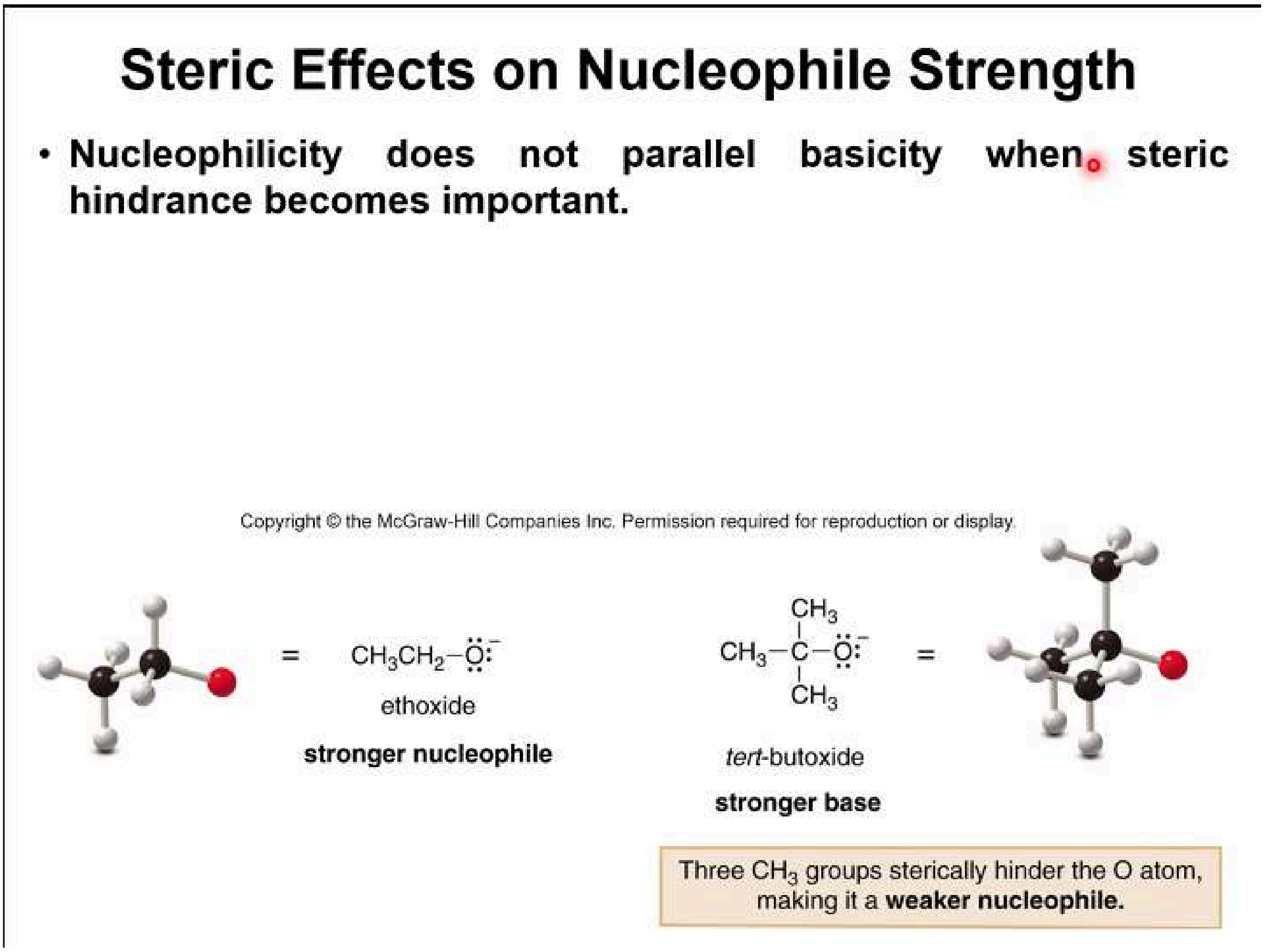
For second-row elements with the same charge:

CH_3^- $^-NH_2$ ^-OH F^-

Increasing basicity
Increasing nucleophilicity

steric effects on nucleophile strength

nucleophilicity does not parallel basicity when steric hindrance becomes important
less steric hindrance, more nucleopphilic



Steric Effects on Nucleophile Strength

- Nucleophilicity does not parallel basicity when steric hindrance becomes important.

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= $CH_3CH_2{-}\ddot{\underset{..}{O}}{:}^-$

ethoxide

stronger nucleophile

$CH_3{-}\underset{CH_3}{\overset{CH_3}{C}}{-}\ddot{\underset{..}{O}}{:}^-$ =

tert-butoxide

stronger base

Three CH_3 groups sterically hinder the O atom, making it a **weaker nucleophile.**

Tert butoxide is a stronger base but weaker nucleophile

steric hindrance, decrease in reactivity resulting from the presence of bulky groups at the site of a reaction
steric hindrance decreases nucleophilicity but not basicity.

Bond breaking and making in nucleophilic substitution mechanisms

overall reaction

Bond Breaking and Making in Nucleophilic Substitution Mechanisms

Overall reaction

$$R{-}X \quad + \quad :Nu^{-} \longrightarrow R{-}Nu \quad + \quad X:^{-}$$

This σ bond is broken. This σ bond is formed.

Bond Breaking and Making in Nucleophilic Substitution Mechanisms

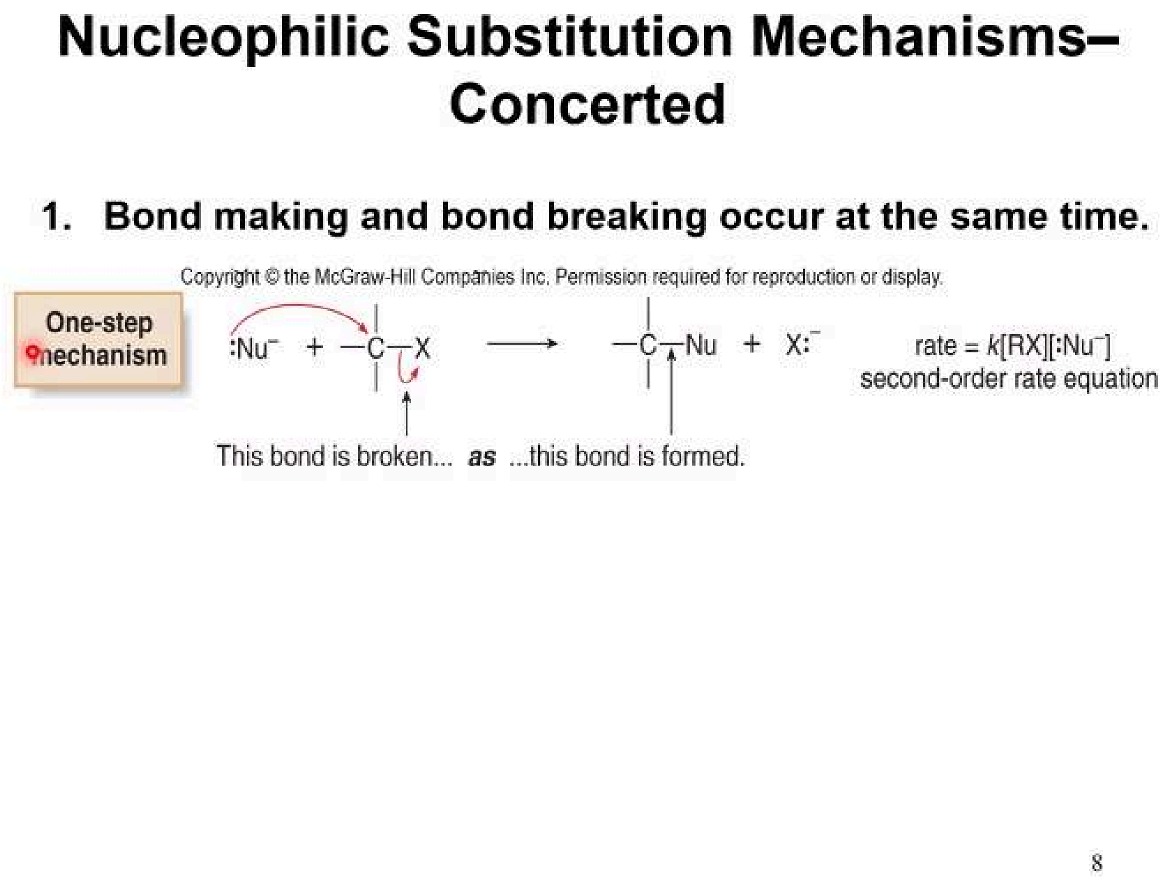
Overall reaction

$$R{-}X \quad + \quad :Nu^{-} \longrightarrow R{-}Nu \quad + \quad X:^{-}$$

This σ bond is broken. This σ bond is formed.

- But what is the order of bond making and bond breaking?
- In theory, there are three possibilities.
  - Bond making and breaking occur at the same time.
  - Bond breaking occurs first.
  - Bond making occurs first.

1. bond making and bond breaking occur at the same time
   one step mechanism



Nucleophilic Substitution Mechanisms–Concerted

1. **Bond making and bond breaking occur at the same time.**

One-step mechanism

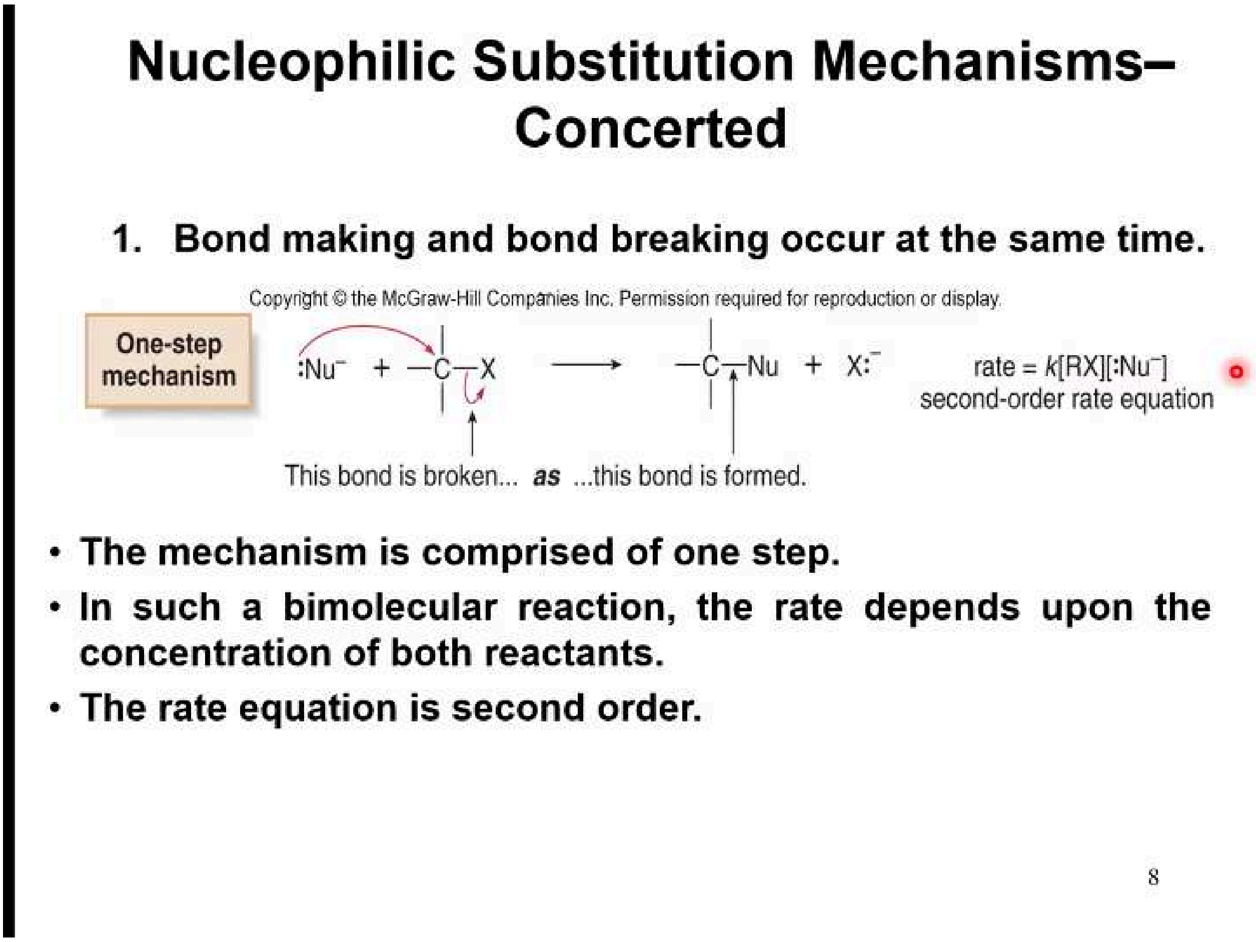
$:Nu^- + -C-X \longrightarrow -C-Nu + X:^-$

This bond is broken... ***as*** ...this bond is formed.

rate = k[RX][:Nu⁻]
second-order rate equation

---

second order rate equation
the mech is one step
bimolecular reaction, the rate depends upon the concentration of both reactants
the rate equation is second order



Nucleophilic Substitution Mechanisms–Concerted

1. Bond making and bond breaking occur at the same time.

One-step mechanism

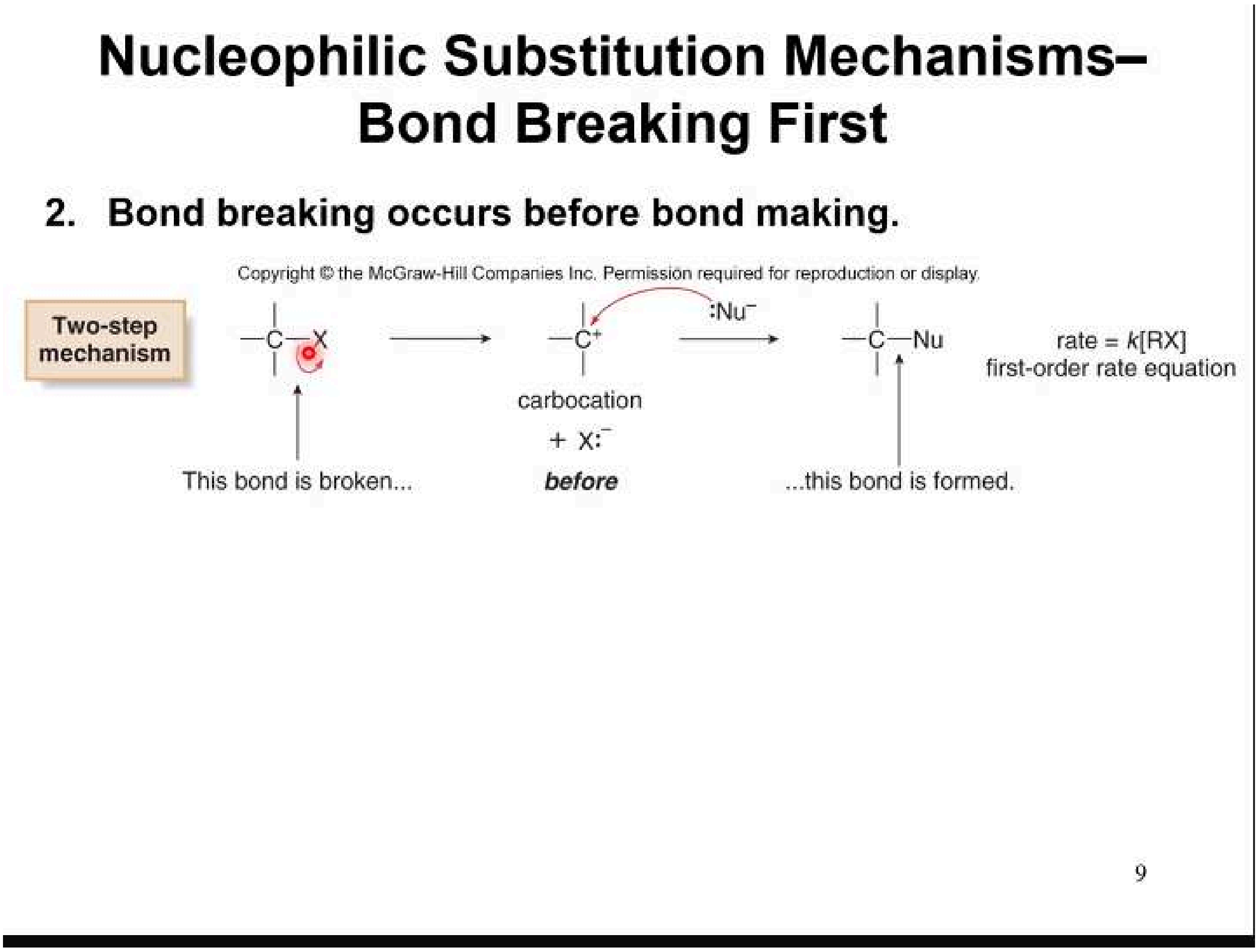
$:Nu^- + -C-X \longrightarrow -C-Nu + X:^-$

rate = $k[RX][:Nu^-]$
second-order rate equation

This bond is broken... *as* ...this bond is formed.

- **The mechanism is comprised of one step.**
- **In such a bimolecular reaction, the rate depends upon the concentration of both reactants.**
- **The rate equation is second order.**

bond breaking occurs before bond making
two step mechanism



Nucleophilic Substitution Mechanisms–Bond Breaking First

2. Bond breaking occurs before bond making.

Two-step mechanism

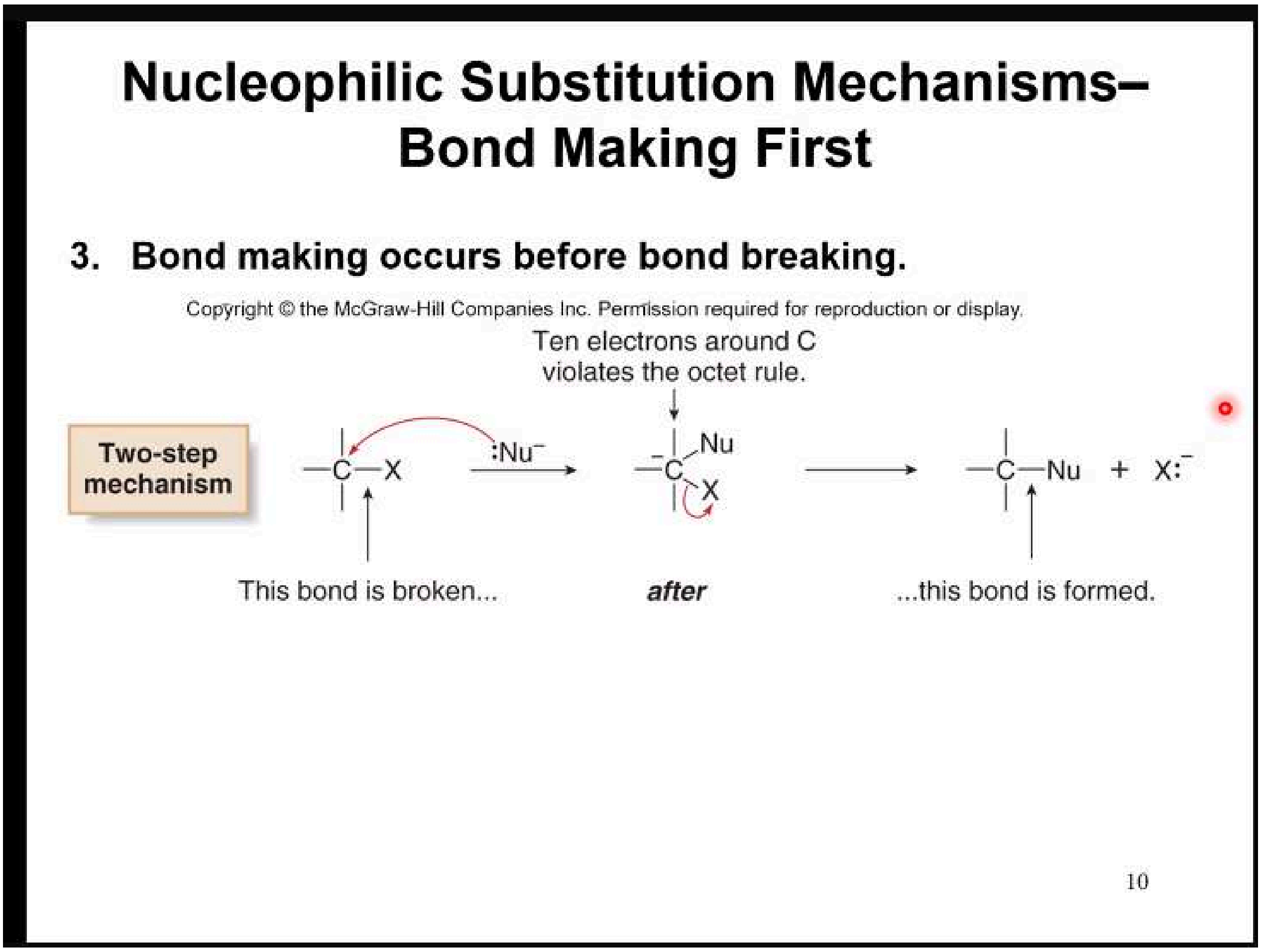
$-C-X \longrightarrow -C^+ \xrightarrow{:Nu^-} -C-Nu$

carbocation
+ $X:^-$

rate = $k[RX]$
first-order rate equation

This bond is broken... ***before*** ...this bond is formed.

rate limiting step - first reaction



Nucleophilic Substitution Mechanisms– Bond Making First

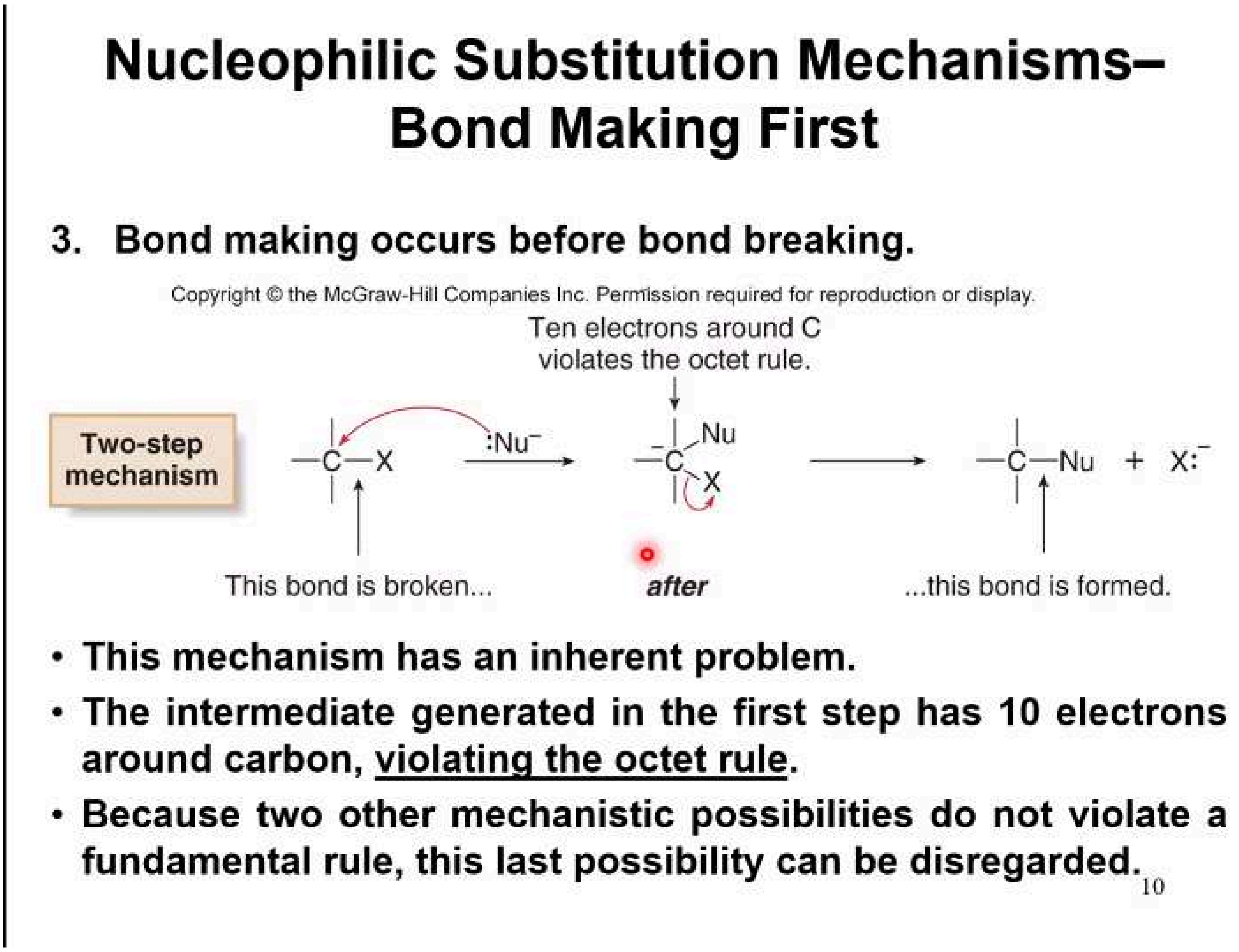
3. Bond making occurs before bond breaking.

Two-step mechanism

Ten electrons around C violates the octet rule.

This bond is broken... *after* ...this bond is formed.

ten electrons around C violates the octet rule
this is why its not allowed



Nucleophilic Substitution Mechanisms– Bond Making First

3. Bond making occurs before bond breaking.

Two-step mechanism

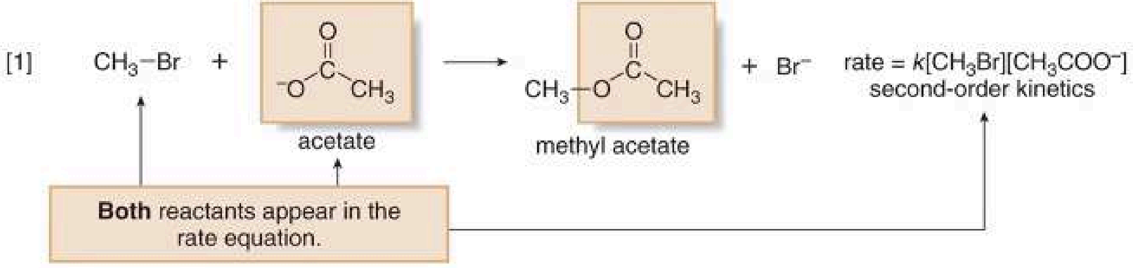
Ten electrons around C violates the octet rule.

This bond is broken... *after* ...this bond is formed.

- **This mechanism has an inherent problem.**
- **The intermediate generated in the first step has 10 electrons around carbon, <u>violating the octet rule</u>.**
- **Because two other mechanistic possibilities do not violate a fundamental rule, this last possibility can be disregarded.**

Kinetics and Mechanisms

Consider reaction 1 below:



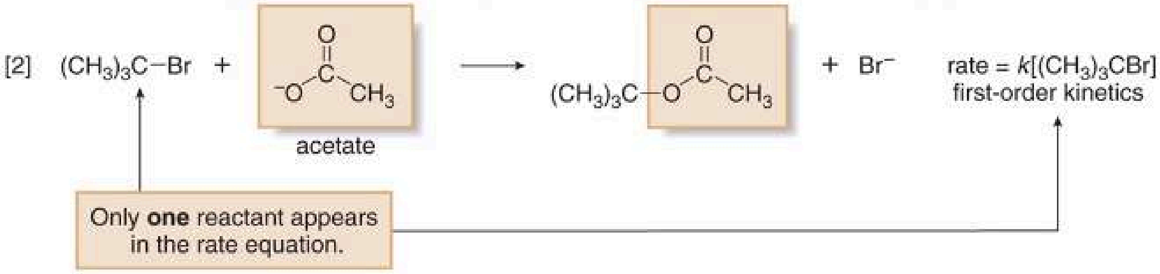
rate = $k[CH_3Br][CH_3COO^-]$
second-order kinetics

Both reactants appear in the rate equation.

- Kinetic data show that the rate of reaction 1 depends on the concentration of both reactants, which suggests a bimolecular reaction with a one-step mechanism.
- This is an example of an S_N2 (substitution nucleophilic bimolecular) mechanism.

Kinetics and Mechanisms

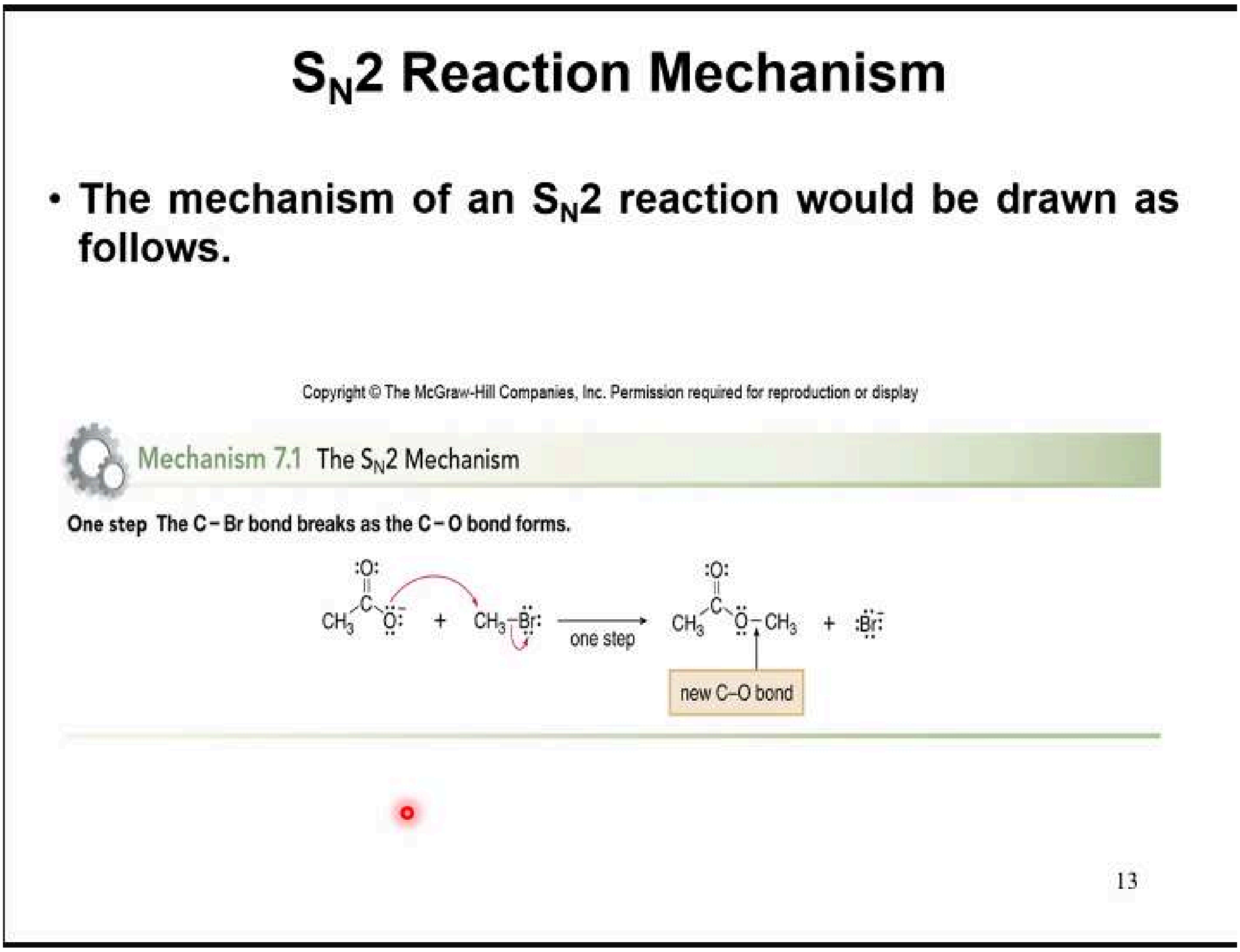
Consider reaction 2 below:



rate = $k[(CH_3)_3CBr]$
first-order kinetics

Only **one** reactant appears in the rate equation.

- Kinetic data show that the rate of reaction 2 depends on the concentration of only the alkyl halide.
- This suggests a two-step mechanism in which the rate-determining step involves the alkyl halide only.
- This is an example of an S_N1 (substitution nucleophilic unimolecular) mechanism.



S_N2 Reaction Mechanism

- The mechanism of an S_N2 reaction would be drawn as follows.

Mechanism 7.1 The S_N2 Mechanism

One step The C – Br bond breaks as the C – O bond forms.

SN2 reactions exhibit 2nd order kinetics

the reaction is bimolecular, both the alkyl halide and the nucleophile appear in the rate equation

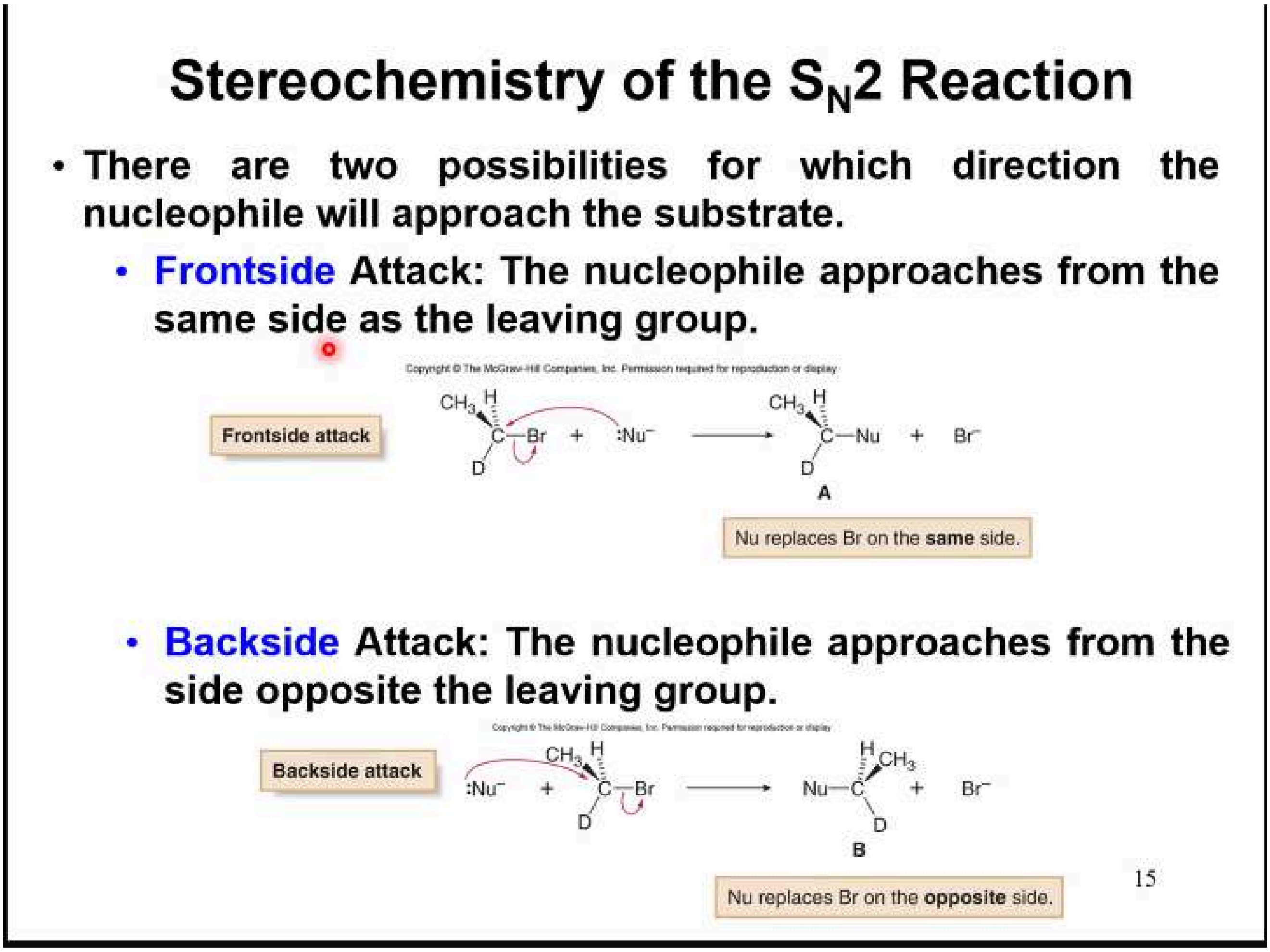
S_N2 Kinetics

- S_N2 reactions exhibit 2nd order kinetics.
- The reaction is bimolecular – both the alkyl halide and the nucleophile appear in the rate equation.

$$\text{rate} = k[CH_3Br][CH_3COO^-]$$

TWO POSSIBILITIES FOR WHICH DIRECTION
FRONTSIDE ATTACK: THE NUCLEOPHILE APPROACHES FROM THE SAME SIDE AS THE LEAVING GROUP
SAME SIDE AS THE LEAVING GROUP

BACKSIDE ATTACK: OPPOSITE SIDE AS THE LEAVING GROUP
INVERSION OF STEREOCHEM



Stereochemistry of the S_N2 Reaction

- There are two possibilities for which direction the nucleophile will approach the substrate.
  - **Frontside** Attack: The nucleophile approaches from the same side as the leaving group.

Frontside attack

Nu replaces Br on the **same** side.

  - **Backside** Attack: The nucleophile approaches from the side opposite the leaving group.

Backside attack

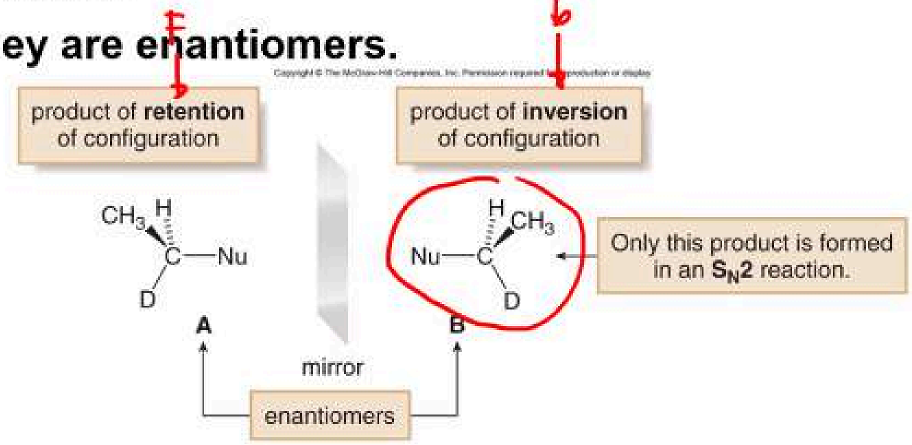
Nu replaces Br on the **opposite** side.

backside think of car

backside para di mataaman sa parking

Stereochemistry of the S_N2 Reaction

- The products of frontside and backside attack are different compounds.
  - They are enantiomers.

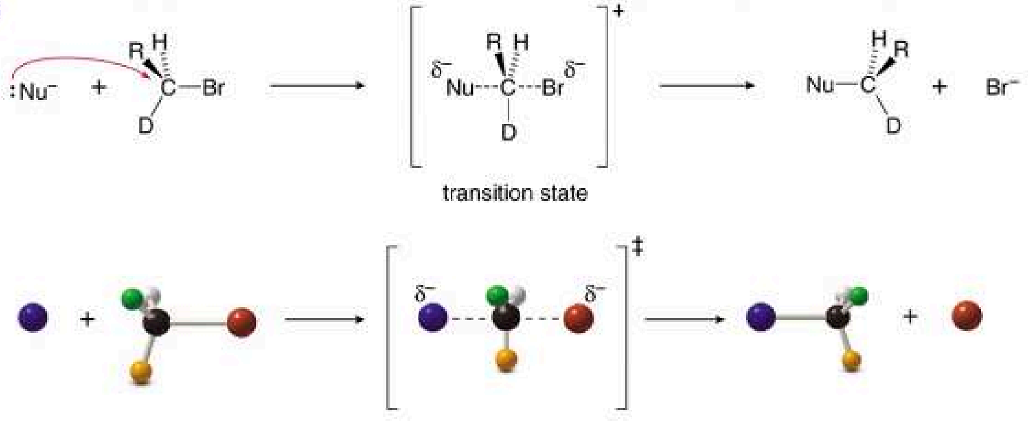


- All S_N2 reactions proceed with backside attack of the nucleophile.
- They result in inversion of configuration at the stereocenter.

Transition States of S_N2 Reactions

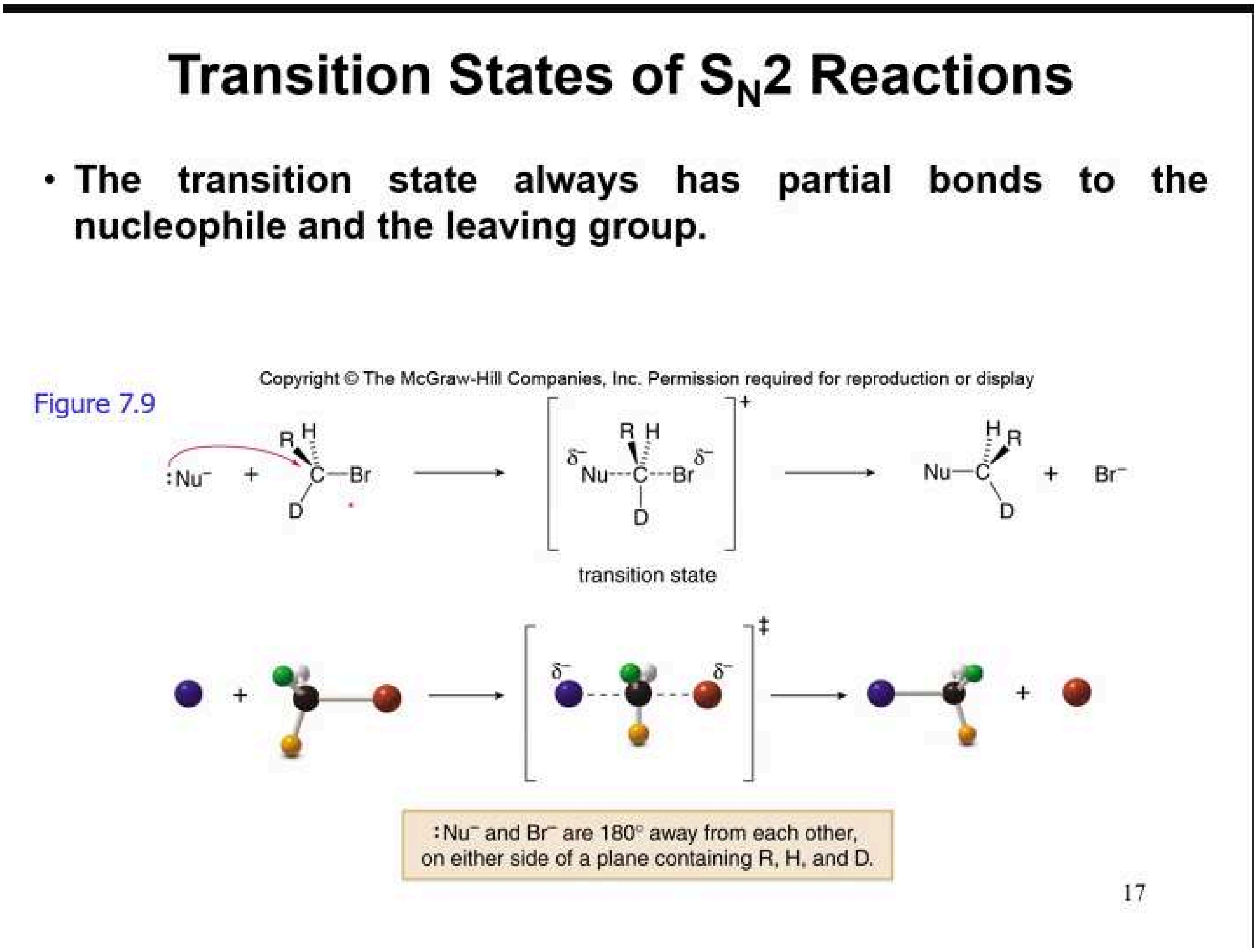
- The transition state always has partial bonds to the nucleophile and the leaving group.

Figure 7.9



:Nu⁻ and Br⁻ are 180° away from each other, on either side of a plane containing R, H, and D.

transittion state always has partial bonds to the nucleophile and the leaving group



Transition States of S_N2 Reactions

- The transition state always has partial bonds to the nucleophile and the leaving group.

Figure 7.9

:Nu⁻ and Br⁻ are 180° away from each other, on either side of a plane containing R, H, and D.

Nu and BR are 180 away from each other
on either side of a plane containing R H AND D

Inversion in S_N2 Reactions

Figure 7.10

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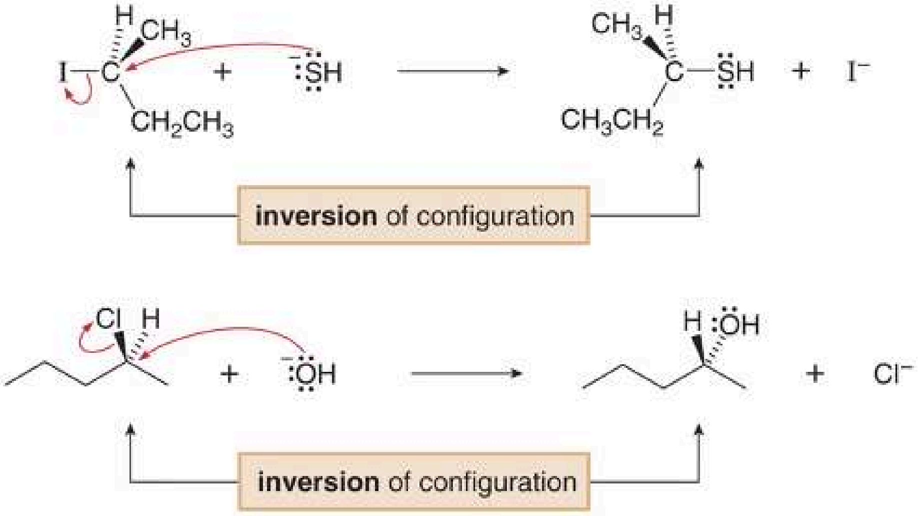
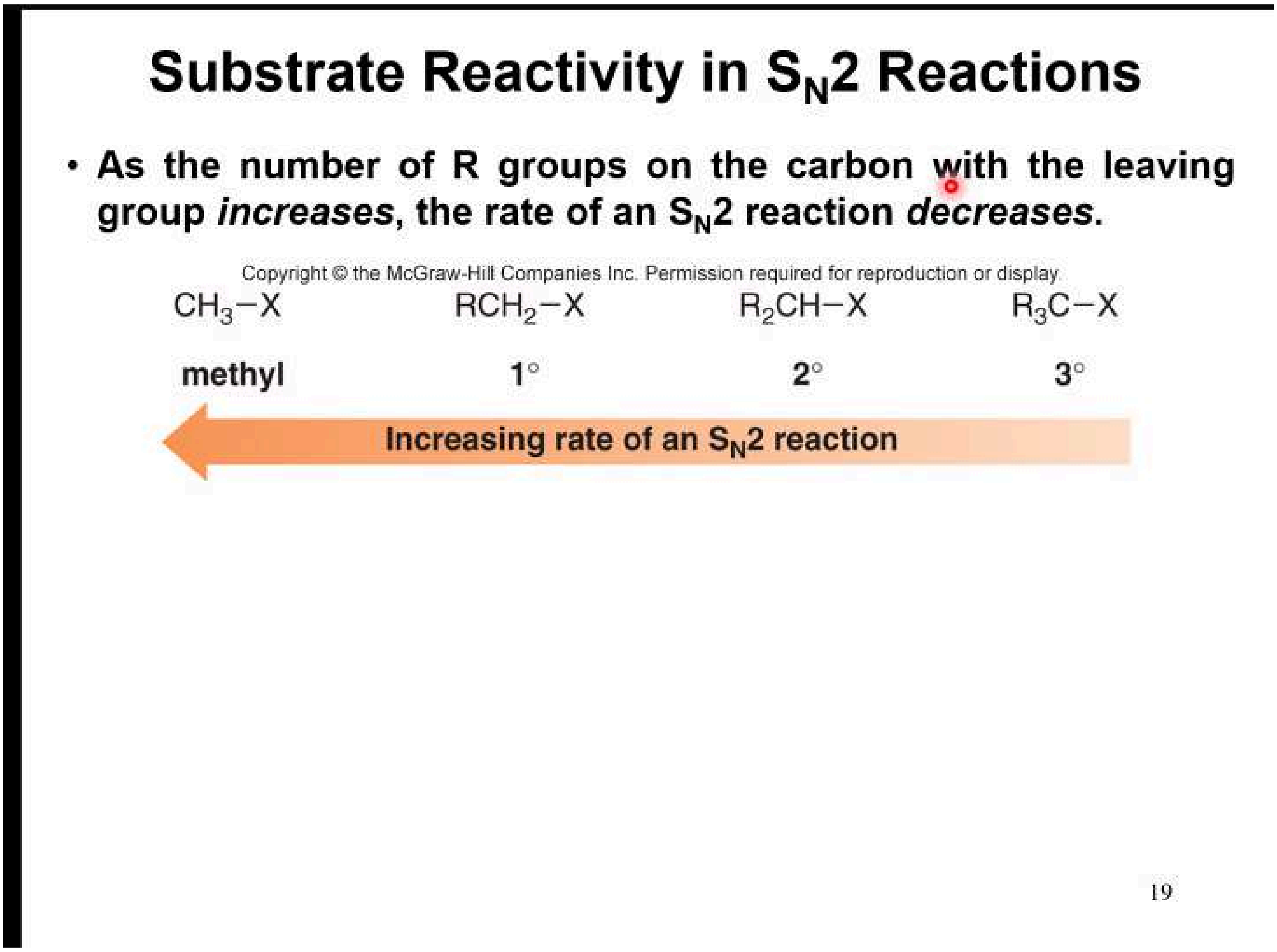


Substrate reactivity in SN2 reactions

as the number of R groups on the carbon with the leaving group increases, the rate of an SN2 reaction decreases



Substrate Reactivity in S_N2 Reactions

- As the number of R groups on the carbon with the leaving group *increases*, the rate of an S_N2 reaction *decreases*.

$CH_3{-}X$	$RCH_2{-}X$	$R_2CH{-}X$	$R_3C{-}X$
methyl	**1°**	**2°**	**3°**

Increasing rate of an S_N2 reaction

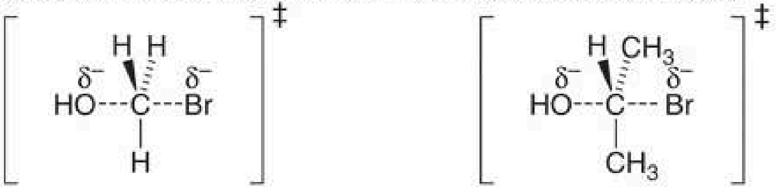
METHYL AND 1 ALKYL HALIDES UNDERGO SN2 WITH EASE
2 ALKYL HALIDES REACT SLOWLY
3 ALKYL HJALIDES DO NOT GO SN2 REACTIONS DUE TO STERIC EFFECTS

BULKYL R GROUPS NEAR THE REACTION SITE MAKE NUCLEOPHILE ATTACK FROM THE BACKSIDE MORE DIFFICULT SLOWING THE REACTOINR ATE

LESS THINGS - EASIER
more r more crowd harder

Effect of Sterics on Rate of S_N2 Reactions

- Increasing the number of R groups on the carbon with the leaving group increases crowding in the transition state, thereby decreasing the reaction rate.
- The S_N2 reaction is fastest with unhindered halides.



less crowded transition state
lower in energy

faster S_N2 reaction

more crowded transition state
higher in energy

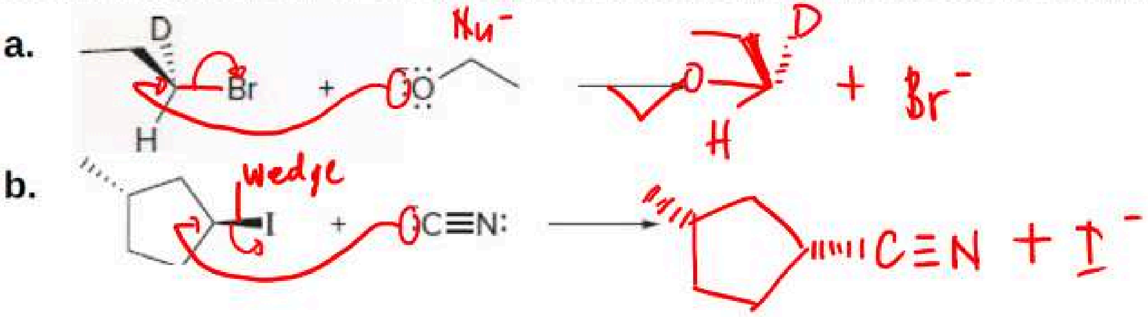
slower S_N2 reaction

Characteristics of the S_N2 Mechanism

Table 7.5 Characteristics of the S_N2 Mechanism

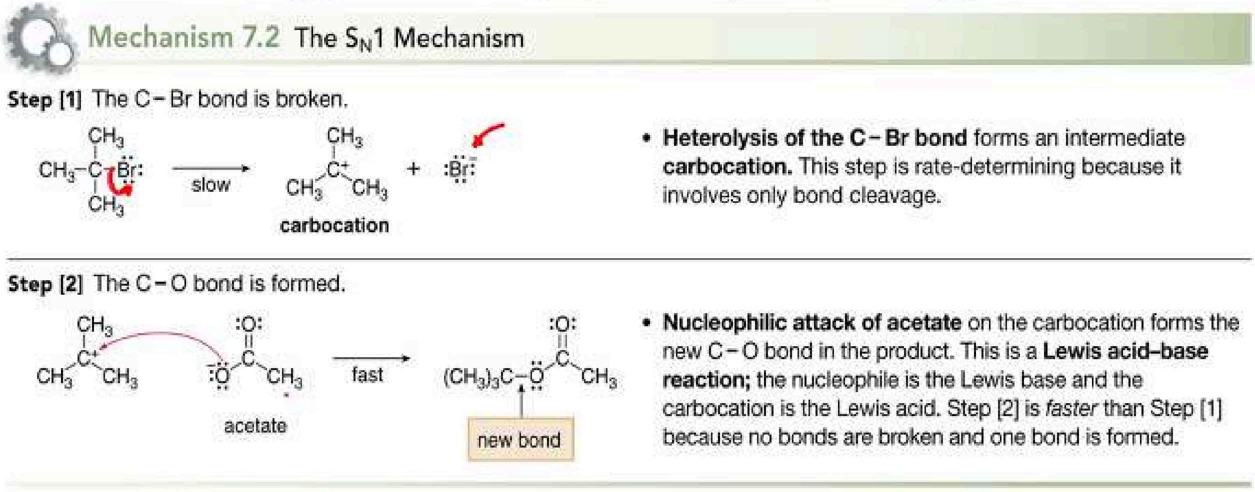
Characteristic	Result
Kinetics	• Second-order kinetics; rate = $k[RX][:Nu^-]$
Mechanism	• One step
Stereochemistry	• Backside attack of the nucleophile • Inversion of configuration at a stereogenic center
Identity of R	• Unhindered halides react fastest. • Rate: $CH_3X > RCH_2X > R_2CHX > R_3CX$

Draw the product of each S_N2 reaction and indicate stereochemistry.



S_N1 Reaction Mechanism

- **The mechanism of an S_N1 reaction would be drawn as follows: Note the curved arrow formalism that is used to show the flow of electrons.**



Mechanism 7.2 The S_N1 Mechanism

Step [1] The C–Br bond is broken.

- **Heterolysis of the C–Br bond** forms an intermediate **carbocation.** This step is rate-determining because it involves only bond cleavage.

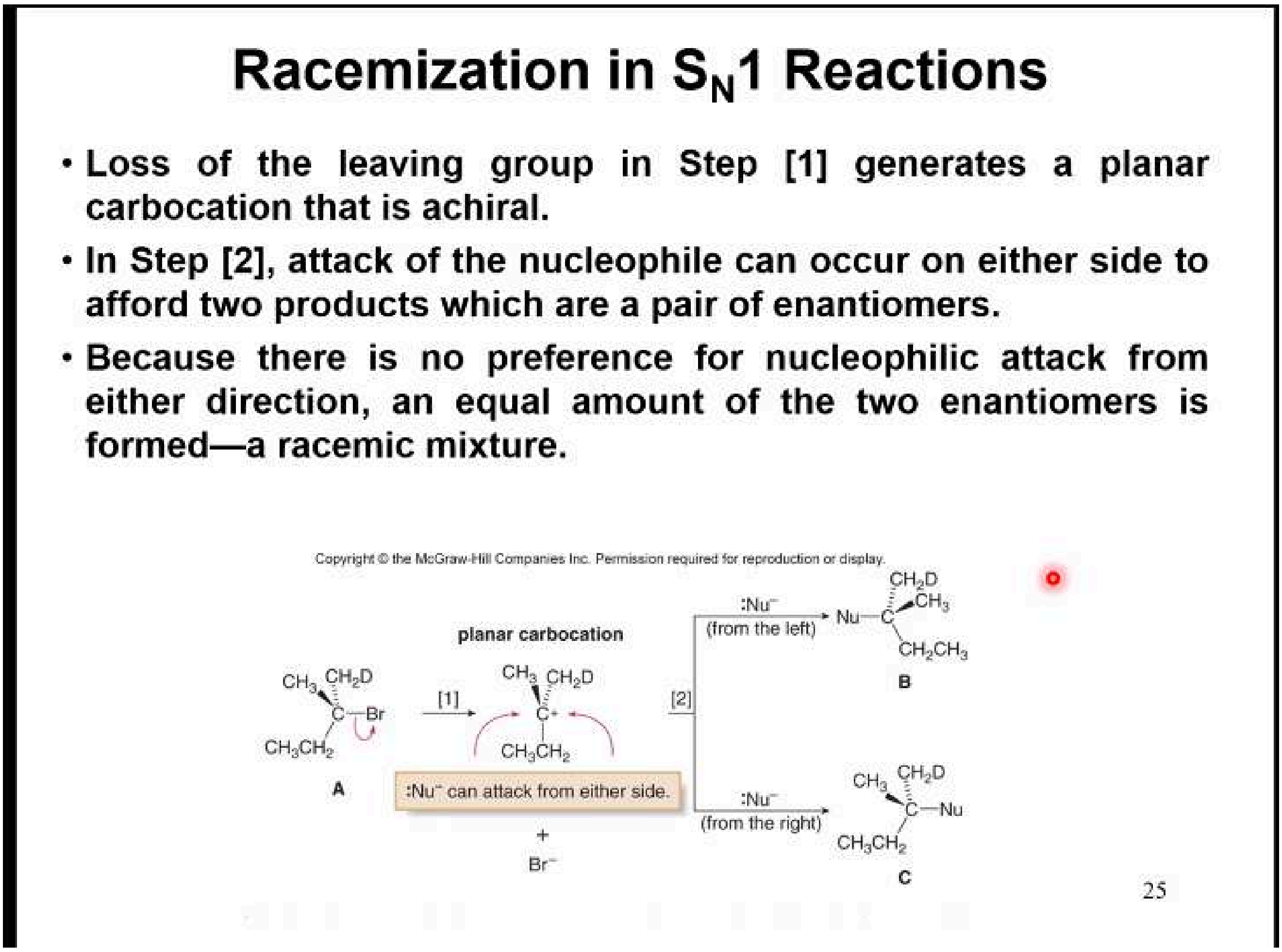
Step [2] The C–O bond is formed.

- **Nucleophilic attack of acetate** on the carbocation forms the new C–O bond in the product. This is a **Lewis acid–base reaction;** the nucleophile is the Lewis base and the carbocation is the Lewis acid. Step [2] is *faster* than Step [1] because no bonds are broken and one bond is formed.

Factor	Favors SN1	Favors SN2
Substrate	Tertiary (3°), secondary (2°), allylic, benzylic	Methyl, primary (1°), secondary (2°)
Nucleophile	Weak	Strong
Leaving Group	Good	Good
Solvent	Polar protic (e.g., H_2O, ROH)	Polar aprotic (e.g., acetone, DMSO, DMF)
Mechanism	Two-step (carbocation intermediate)	One-step (concerted, backside attack)
Stereochemistry	Racemization (if chiral center)	Inversion of configuration (Walden inversion)

SN1 EXHIBIT 1ST ORDER KINETICS
THE REACTION IS UNIMOLECULAR INVOLVING ONLY THE ALKYL HALIDE
THE IDENITTY AND CONCENTRATION OF THE NUCLEOPHILE HAVE NO EFFECT ON TH REACTION RATE
THEREFORE THE NUCLEOPHILE DOES NOT APPEAR IN THE RATE EQUATION
ONLY THE CONCENTRATION LEAVING GROUP IS IN THE RATE

LOSS OF THE LEAVING GROUP IN STEP 1 GENERATES A PLANAR CARBOCATION THAT IS ACHIRAL
IN STEP 2 ATTACK OF THE NUCLEOPHILE CAN OCCUR ON EITHER SIDE TOA FFORD TWO PRODCUTS WHICH ARE A PAIR OF ENANTIOMERS



Racemization in S_N1 Reactions

- Loss of the leaving group in Step [1] generates a planar carbocation that is achiral.
- In Step [2], attack of the nucleophile can occur on either side to afford two products which are a pair of enantiomers.
- Because there is no preference for nucleophilic attack from either direction, an equal amount of the two enantiomers is formed—a racemic mixture.

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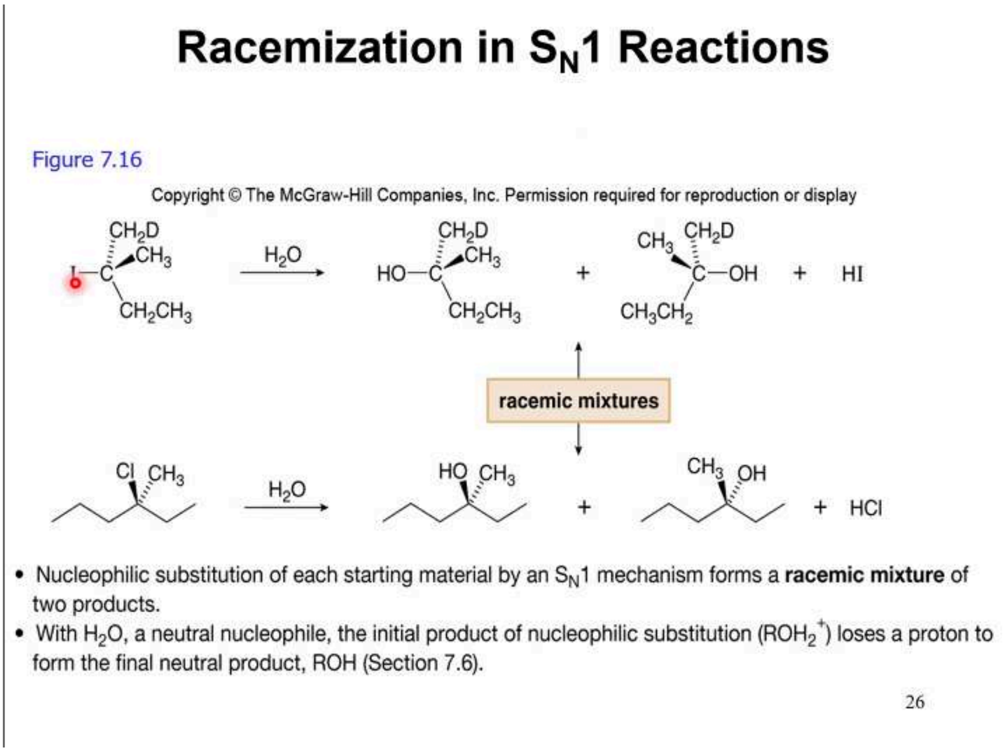
EQUAL AMOUNT = RACEMIC

THIS IS CALLED RACEMIZATION

CAN DO BACK AND FRONTSIDE ATTACK



Racemization in S_N1 Reactions

Figure 7.16

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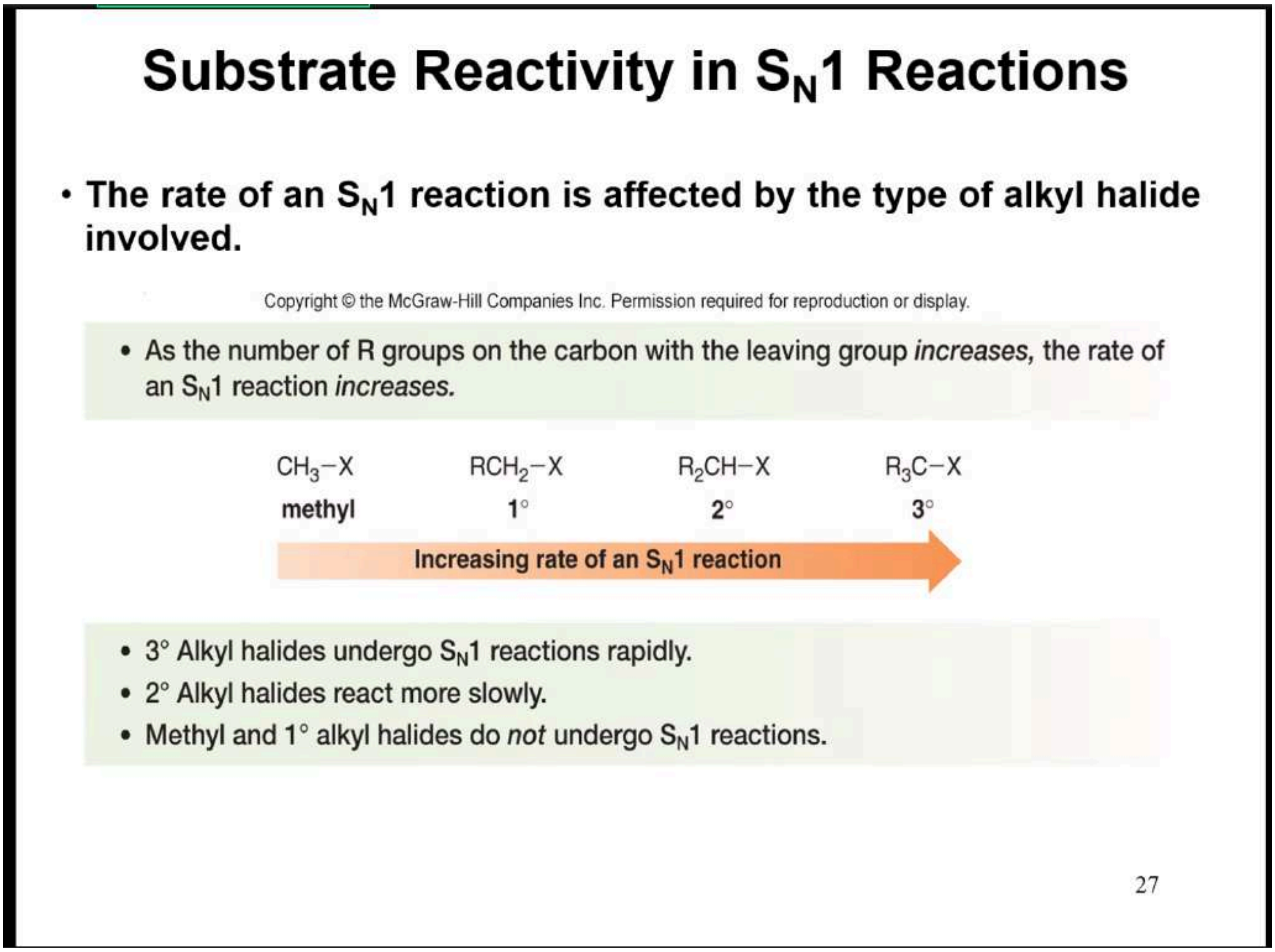
- Nucleophilic substitution of each starting material by an S_N1 mechanism forms a **racemic mixture** of two products.
- With H_2O, a neutral nucleophile, the initial product of nucleophilic substitution (ROH_2^+) loses a proton to form the final neutral product, ROH (Section 7.6).



Substrate Reactivity in S_N1 Reactions

- **The rate of an S_N1 reaction is affected by the type of alkyl halide involved.**

- As the number of R groups on the carbon with the leaving group *increases,* the rate of an S_N1 reaction *increases.*

CH_3-X	RCH_2-X	R_2CH-X	R_3C-X
methyl	**1°**	**2°**	**3°**

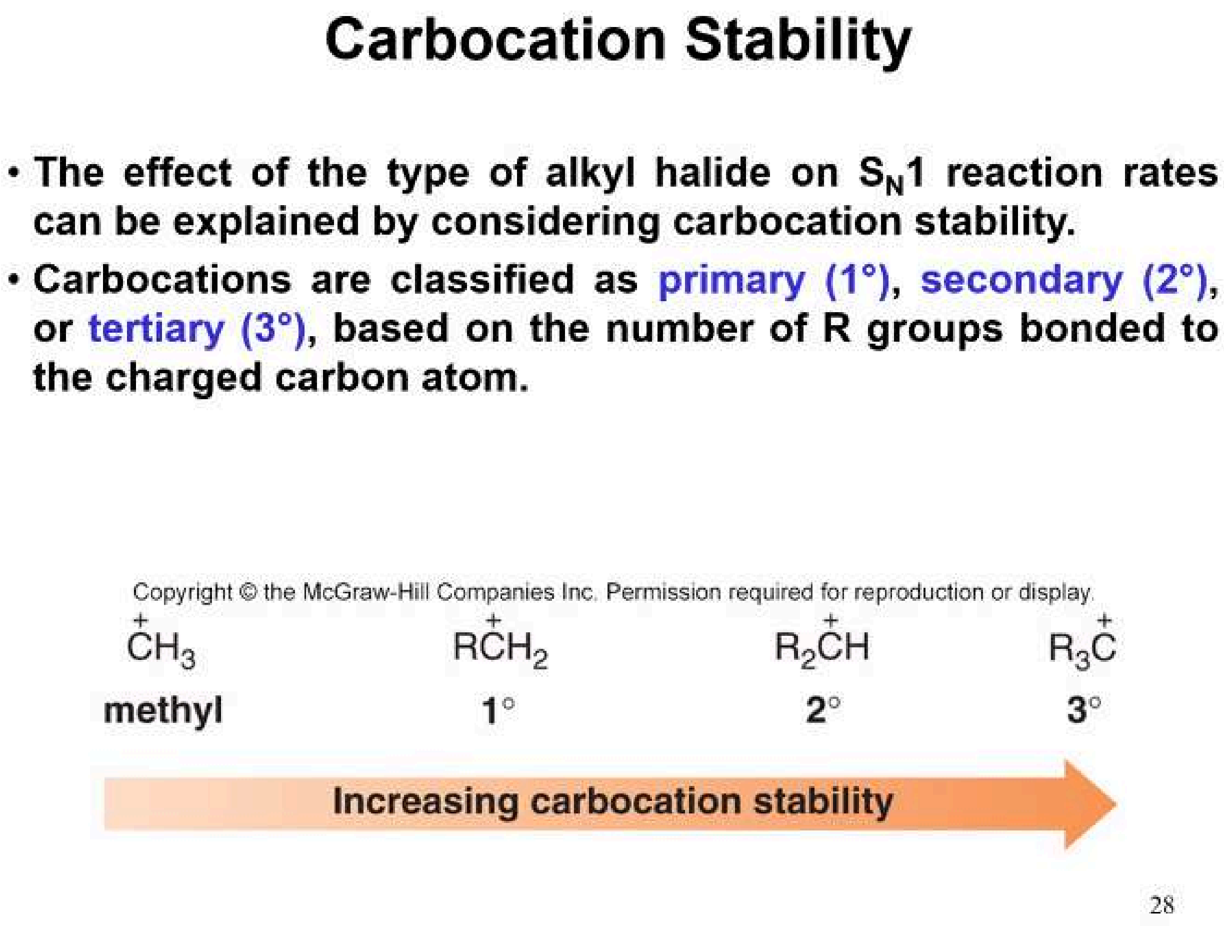
Increasing rate of an S_N1 reaction

- 3° Alkyl halides undergo S_N1 reactions rapidly.
- 2° Alkyl halides react more slowly.
- Methyl and 1° alkyl halides do *not* undergo S_N1 reactions.

opposite of SN2

CARBOCATION STABILITY

THE EFFECT OF THE TYPE OF ALKYL HALIDE ON SN1 REACTION RATES CAN BE EXPLAINED BY CONSIDERING CARBOCATION STABILITY



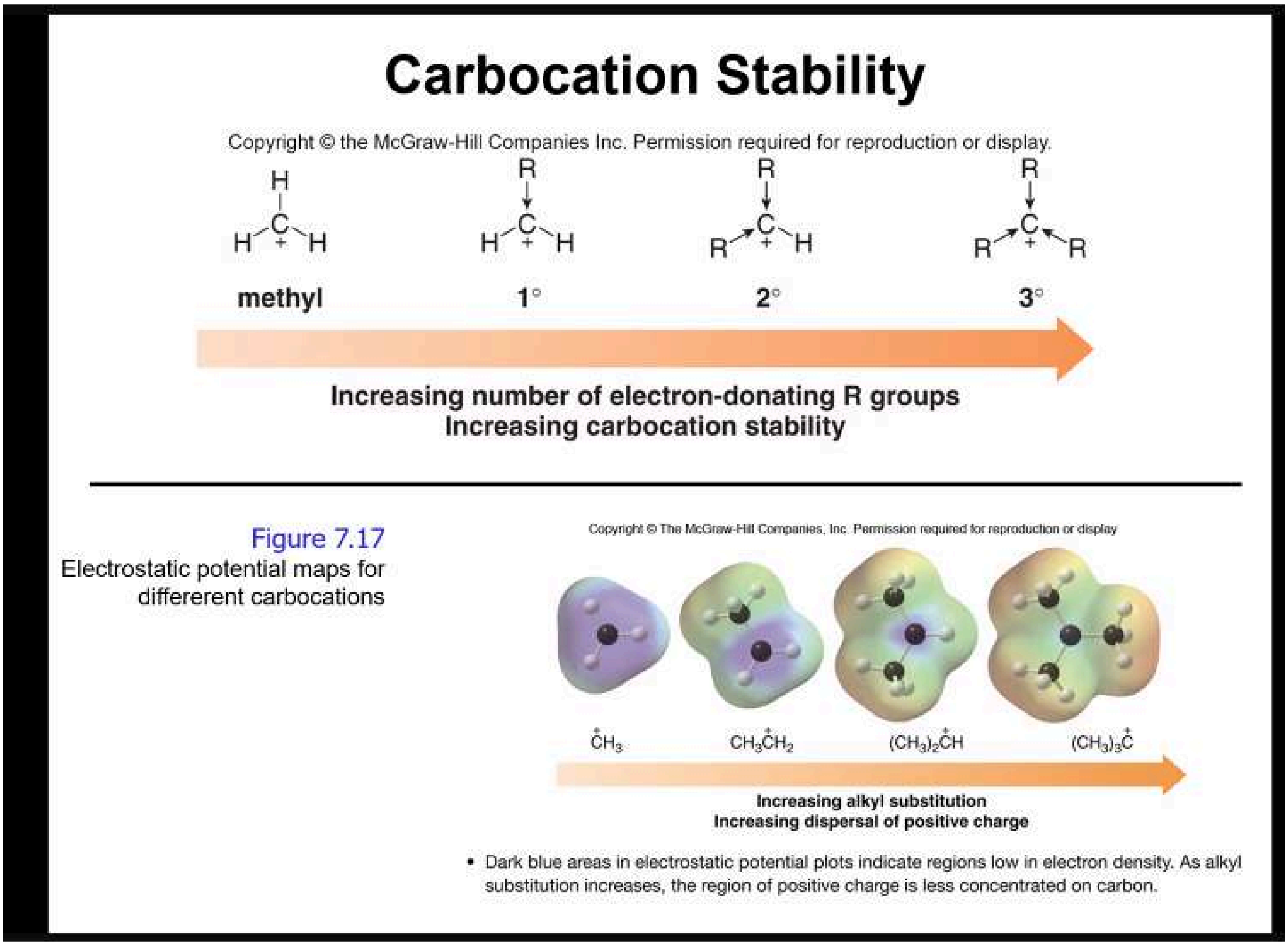
Carbocation Stability

- The effect of the type of alkyl halide on S_N1 reaction rates can be explained by considering carbocation stability.
- Carbocations are classified as primary (1°), secondary (2°), or tertiary (3°), based on the number of R groups bonded to the charged carbon atom.

$\overset{+}{C}H_3$	$R\overset{+}{C}H_2$	$R_2\overset{+}{C}H$	$R_3\overset{+}{C}$
methyl	**1°**	**2°**	**3°**

Increasing carbocation stability

the order of carbocation stability can be rationalized through inductive effects and hyperconjugation
inductive effects pull of elec dens through sigma bonds caused by ele neg diff between atoms
alkyl groups are electrond onor groups
as a result, alkyl are more polarizable than a hydro atom
more alkyl groups attached to carbon with pos charge, more stable cation



Carbocation Stability

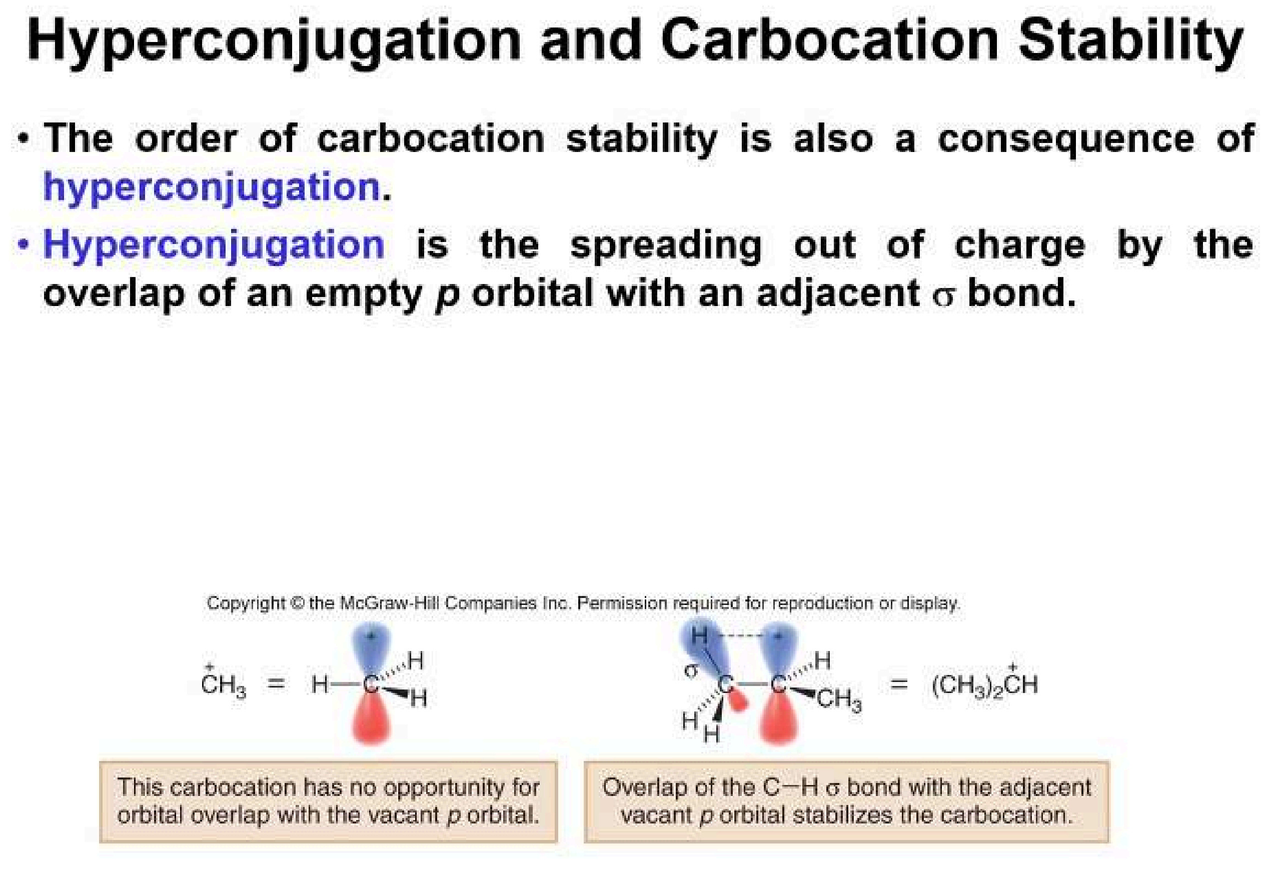
Increasing number of electron-donating R groups
Increasing carbocation stability

Figure 7.17
Electrostatic potential maps for differerent carbocations

$\overset{+}{C}H_3$ $CH_3\overset{+}{C}H_2$ $(CH_3)_2\overset{+}{C}H$ $(CH_3)_3\overset{+}{C}$

Increasing alkyl substitution
Increasing dispersal of positive charge

- Dark blue areas in electrostatic potential plots indicate regions low in electron density. As alkyl substitution increases, the region of positive charge is less concentrated on carbon.



Hyperconjugation and Carbocation Stability

- The order of carbocation stability is also a consequence of **hyperconjugation**.
- **Hyperconjugation** is the spreading out of charge by the overlap of an empty *p* orbital with an adjacent σ bond.

This carbocation has no opportunity for orbital overlap with the vacant *p* orbital.

Overlap of the C—H σ bond with the adjacent vacant *p* orbital stabilizes the carbocation.

Carbocation stability is a critical factor that dictates whether an SN1 or SN2 reaction is favored for a given substrate.1 Let's break down why.

What is a Carbocation?

A **carbocation** is an organic ion in which a carbon atom bears a positive charge and has only three bonds, giving it an incomplete octet (six valence electrons).2 It is sp2-hybridized and has a trigonal planar geometry, with an empty p-orbital perpendicular to the plane.3 Because it lacks a full octet and carries a positive charge, carbocations are highly reactive and unstable species.4

Factors Affecting Carbocation Stability

The stability of a carbocation is crucial because the formation of a carbocation is the rate-determining step in SN1 reactions.5 Anything that can help to delocalize or stabilize this positive charge will make the carbocation more stable and thus accelerate its formation.6

The general order of carbocation stability is:

Allylic ~ Benzylic (most stable due to resonance) > Tertiary (3°) > Secondary (2°) > Primary (1°) > Methyl (least stable)

Here's why:

1. **Inductive Effect:**
    - Alkyl groups (methyl, ethyl, etc.) are **electron-donating groups** via the inductive effect. They can push electron density towards the positively charged carbon, which helps to spread out and neutralize the positive charge.
    - The more alkyl groups attached to the positively charged carbon, the more electron density can be donated, and the more stable the carbocation becomes.
    - Therefore, a tertiary carbocation (carbon bonded to three other alkyl groups) is more stable than a secondary (two alkyl groups), which is more stable than a primary (one alkyl group), and a methyl carbocation (no alkyl groups) is the least stable.7
2. **Hyperconjugation:**
    - Hyperconjugation is the stabilizing interaction between a filled C-H (or C-C) sigma (8σ) bond on an adjacent carbon and the empty p-orbital of the carbocation.9
    - Electrons from these 10σ bonds can partially delocalize into the empty p-orbital, effectively sharing electron density with the positively charged carbon.11
    - The more C-H or C-C bonds adjacent to the carbocation (i.e., the more alkyl groups), the greater the number of hyperconjugation interactions, and thus the greater the stability.12 This is another reason why tertiary carbocations are more stable.
3. **Resonance Stabilization:**
    - Carbocations can be significantly stabilized if the positive charge can be delocalized through **resonance**.13 This occurs when the carbocation is adjacent to a pi (14π) bond (like in an alkene or aromatic ring) or an atom with a lone pair of electrons.15
    - **Allylic carbocations** (positive charge adjacent to a C=C double bond) and **benzylic carbocations** (positive charge adjacent to an aromatic ring) are highly stable

because the positive charge can be distributed over multiple atoms via resonance structures.16 This delocalization makes them even more stable than tertiary alkyl carbocations.

  - Similarly, a carbocation adjacent to an oxygen or nitrogen atom with lone pairs can also be resonance-stabilized.17

Carbocation Stability and its Impact on SN1 vs. SN2

The stability of carbocations plays a **direct and opposing role** in determining whether an SN1 or SN2 reaction will occur:

SN1 (Substitution Nucleophilic Unimolecular)

- **Reliance on Carbocation Formation:** The defining feature of an SN1 reaction is the formation of a carbocation intermediate in the rate-determining step.18
- **Rate-Limiting Step:** The slower the formation of the carbocation, the slower the overall reaction.19
- **Effect of Stability:** The more stable the carbocation that can be formed, the lower the activation energy for its formation, and thus the **faster the SN1 reaction**.20
- **Substrate Reactivity Order (SN1):** Therefore, SN1 reactions are favored by substrates that can form stable carbocations:21
  - **Tertiary (3∘) alkyl halides** are most reactive because they form the most stable tertiary carbocations.
  - **Secondary (2∘) alkyl halides** are less reactive than tertiary but can still undergo SN1.
  - **Primary (221∘) alkyl halides** and **methyl halides** rarely undergo SN1 because the primary and methyl carbocations are too unstable to form.23
  - **Allylic and benzylic halides** are highly reactive in SN1 due to resonance-stabilized carbocations, even if they are formally primary or secondary.24

SN2 (Substitution Nucleophilic Bimolecular)

- **No Carbocation Intermediate:** SN2 reactions proceed through a concerted, one-step mechanism involving a single transition state.25 There is **no carbocation intermediate** formed.
- **Steric Hindrance is Key:** Instead of carbocation stability, the dominant factor in SN2 is **steric hindrance** at the carbon atom undergoing substitution. The nucleophile must be able to attack the backside of the carbon atom and simultaneously displace the leaving group.
- **Effect of Substitution:** Bulky groups around the electrophilic carbon hinder the backside attack of the nucleophile.
- **Substrate Reactivity Order (SN2):** Therefore, SN2 reactions are favored by substrates with less steric hindrance:26

- **Methyl halides** are most reactive because they have the least steric hindrance.
- **Primary (271◦) alkyl halides** are highly reactive.28
- **Secondary (2◦) alkyl halides** are less reactive than primary and often face competition from SN1 if carbocation stability is also a factor.
- **Tertiary (3◦) alkyl halides** do not undergo SN2 reactions because the steric bulk of the three alkyl groups completely blocks the backside attack by the nucleophile.

In summary, carbocation stability is the cornerstone for predicting SN1 reactivity, while steric hindrance is the main determinant for SN2 reactivity. These two factors often lead to opposite trends in reactivity for different types of alkyl halides.

Characteristics of the S_N1 Mechanism

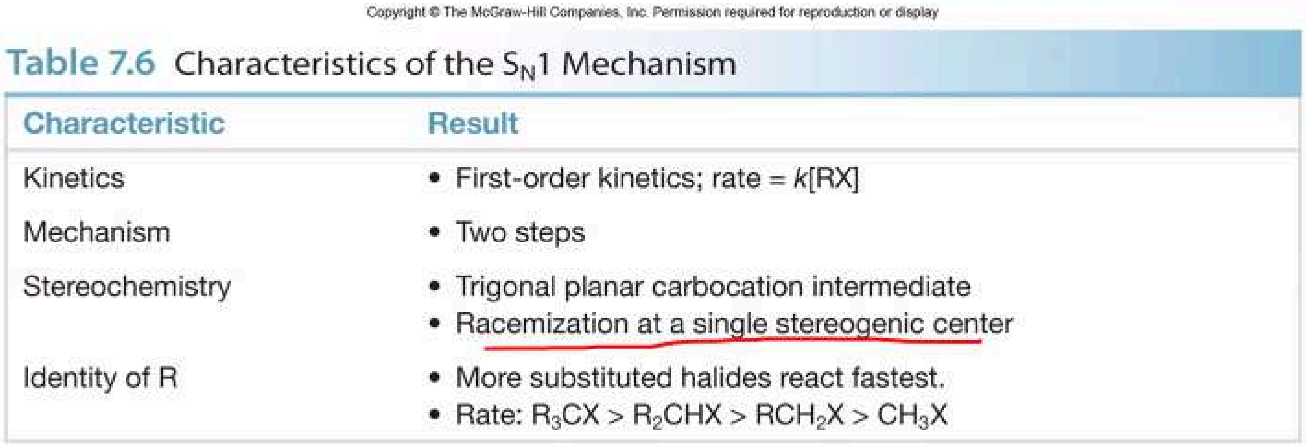


Table 7.6 Characteristics of the S_N1 Mechanism

Characteristic	Result
Kinetics	• First-order kinetics; rate = k[RX]
Mechanism	• Two steps
Stereochemistry	• Trigonal planar carbocation intermediate • Racemization at a single stereogenic center
Identity of R	• More substituted halides react fastest. • Rate: $R_3CX > R_2CHX > RCH_2X > CH_3X$