TOPIC 3. ALKANES

OBJECTIVES

1. Develop rules for systematic nomenclature of alkanes alkenes and alkynes
2. Describe the geometry of hydrocarbons
3. Describe the rotation around C-C single bonds (conformation)
4. Describe the geometry of cyclic alkanes
5. Describe reactions involving alkanes.

PHYSICAL PROPERTIES OF ALKANES

C1-C4: gas   C5-C15: liquid   >C16: solid   large n: polyethylene

Branching *usually* decreases m.p.:
- branches impede crystal packing.
  (Highly symmetric molecules have *higher* m.p.
    e.g., $C(CH_3)_4$, m.p.=-16 °C; $CH_3(CH_2)_3CH_3$, m.p.=-130 °C)

Branching decreases b.p.:
- More compact structure gives less surface area: weaker van der Waals interactions

Non-polar: immiscible with water

Less dense than water

Dissolve other non-polar organic molecules

Flammable!

Chemically inert

Uses: fuels, solvents, waxes

PE-HD

SYSTEMATIC IUPAC NOMENCLATURE OF ALKANES

Linear (Unbranched) Alkanes

|				
CH_4	C1	methane	11	
CH_3CH_3	2	ethane	12	
$CH_3CH_2CH_3$	3	propane	13	
$CH_3(CH_2)_2CH_3$	4	butane	14	
$CH_3(CH_2)_3CH_3$	5	pentane	15	pentadecane
$CH_3(CH_2)_4CH_3$	6		16	hexadecane
$CH_3(CH_2)_5CH_3$	7		17	heptadecane
$CH_3(CH_2)_6CH_3$	8		18	octadecane
$CH_3(CH_2)_7CH_3$	9		19	nondecane
$CH_3(CH_2)_8CH_3$	10		20	eicosane

Branched alkanes

e.g.,
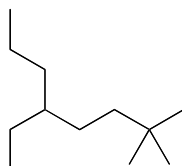
find longest continuous chain of carbons
  base name = alkane

List substituents as prefixes in alphabetical order (ignoring di, tri, *sec*, *tert*;
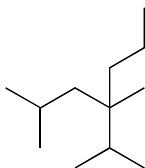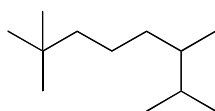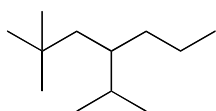but do not ignore "iso")

octane
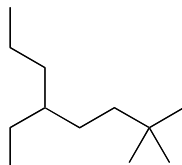
Number longest continuous chain from the end that places a substituent at
the lowest possible number

ethyl   dimethyloctane

e.g.,
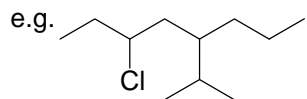
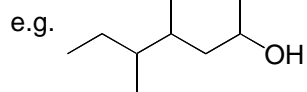*Problem:* Name the following.

NAMING OTHER COMPOUNDS

Alkyl Halides

e.g.

Named as haloalkanes
longest chain
substitutents (incl. halogen) named
Lowest possible position of substituent defines positions

Alcohols

e.g.

Named as alkanols
longest chain
numbered to put –OH in lowest possible position
substitutents named and positions given
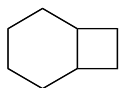
What is the name of the following chloroalkane?

Cl
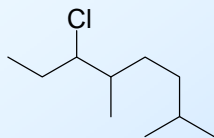
1 4,7-dimethyl-3-chlorooctane

2 2,5-dimethyl-6-chlorooctane

3 6-chloro-2,5-dimethyloctane

4 3-chloro-4,7-dimethyloctane

Bicyclic Alkanes

Named as bicyclo[x,y,z]alkanes

Problem. Name the following bicyclic compounds.

What is the name of the following bicycloalkane?
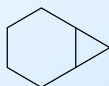
1 bicylco[6.3]hexane

2 bicyclo[4.1.0]heptane

3 bicyclo[6.1.0]heptane

4 bicyclo[6.3.0]propane

Naming Alkenes (and Alkynes)

e.g.,
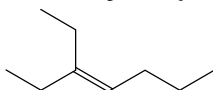
Find longest continuous chain of carbons which contains the C=C (or
C≡C):
base name = alk$\underline{e}$ne (alk$\underline{y}$ne)

Number longest continuous chain of carbons to assign an sp^2 (sp)
carbon to as low a number as possible: #-alkene (#-alkyne)

heptene

Identify substituents and position of substituents. Substituents are listed
alphabetically

3-heptene

Cyclic Alkenes

Define the sp^2 carbons of the alkene as C-1 and C-2 *such that the first encountered substituent occupies the lowest possible number (this is sometimes called the first point of difference rule).*

What about compounds with alcohol and double (or triple) bonds? Consider them alcohols first, and name them as (substituted alkanols)
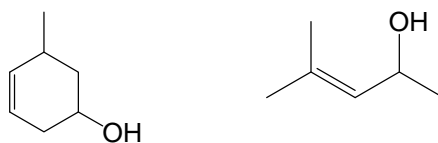
MOLECULAR FORMULA

Alkanes : C_nH_{2n+2}

Alkenes: C_nH_{2n} Cyclic alkanes : C_nH_{2n}

Alkynes: C_nH_{2n-2} Dialkenes: C_nH_{2n-2}

For each ring or pi-bond in a molecule there are two fewer hydrogen atoms than expected for a non-cyclic alkane, so:

Sum of pi bonds and/or rings (SODAR)= (2#C + 2 – #H) / 2

Note: SODAR may also be referred to as "sites of unsaturation" or "index of hydrogen deficiency"

Problems: How many pi bonds or rings are there in C_9H_{14}?

$C_{10}H_{17}$?

The same equation is true in the presence of divalent oxygen or sulfur atoms:

For C,H,O,S: $SODAR = (2\#C + 2 - \#H) / 2$

In the presence of halogens (monovalent) or nitrogen (trivalent):

For C,H,O,N,S, Hal: $SODAR = (2\#C + 2 - \#H - \#Hal + \#N) / 2$

(each Hal replaces a H; each N adds an extra H; and S,O have no effect on the calculation)

Problem: Determine the value of SODAR for compounds with the following molecular formulas.

                    SODAR

C_6H_6

CH_3Br

CH_5N

C_3H_8N

Differentiating alkenes and cycloalkanes

Catalytic hydrogenation

$$\text{H}_2/\text{Pt} \longrightarrow$$

$$\text{H}_2/\text{Pt} \longrightarrow$$
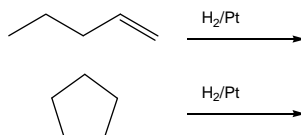
Problem. Compound **A**, C_4H_6, undergoes hydrogenation to afford C_4H_{10}.
  (a) How many rings are present in **A**?
  (b) How many pi bonds?
  (c) Draw all of the possible structures of **A**.

CONFORMATIONAL ANALYSIS:
ROTATION AROUND C-C SINGLE BONDS

Rotation around C-C single bonds leads to formation of different *conformers*.

The energy required to interconvert conformers is small: Conformers can rarely be isolated at room temperature.
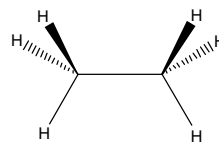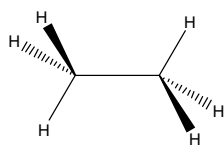
Newman
Projections
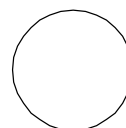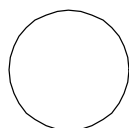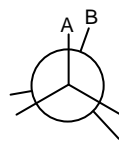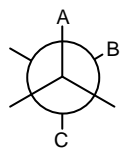
The eclipsing conformation of ethane is destabilized by torsional strain.
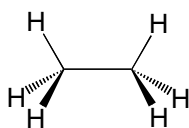
The eclipsing conformations of butane are further destabilized by steric strain
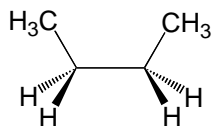
Ethane
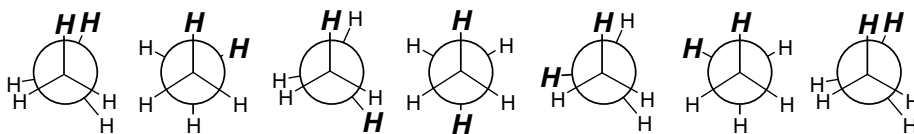
Dihedral angle:

$\Phi=$
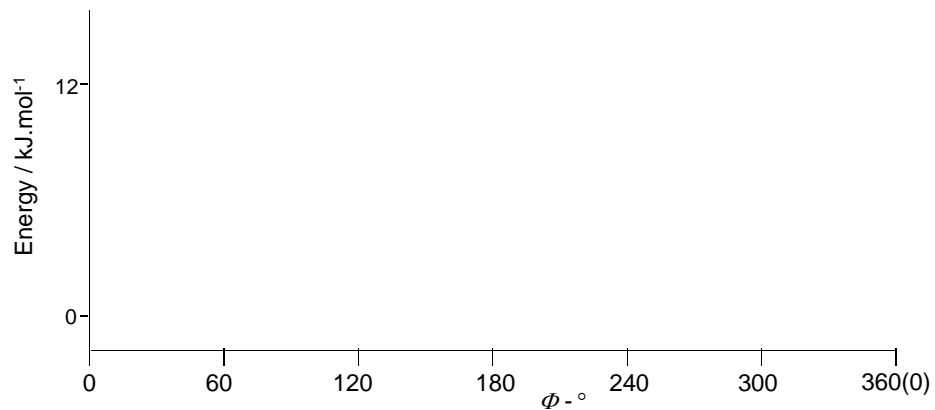
Butane
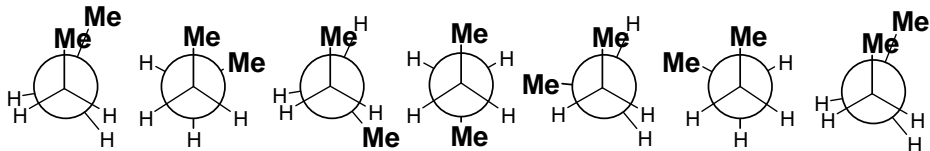
Dihedral angle:

$\Phi=$
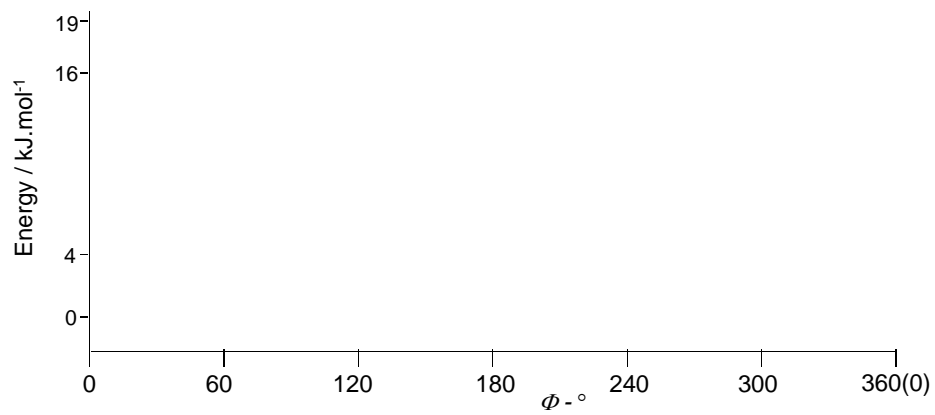
RELATIVE STABILITY
OF CYCLOALKANES

Ring strain: Heat of combustion *per methylene unit* in cycloalkane

n	$\Delta H_c/n$ - kJ/mol per carbon
3	-697
4	-686
5	-664
6	*-659*

$$(CH_2)_n + {}^{3n}/_2 O_2 \xrightarrow{\Delta H_c} n CO_2 + n H_2O$$
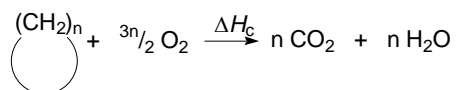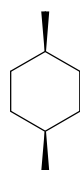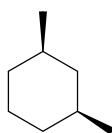
CONFORMATIONAL ANALYSIS OF
SUBSTITUTED CYCLOHEXANES

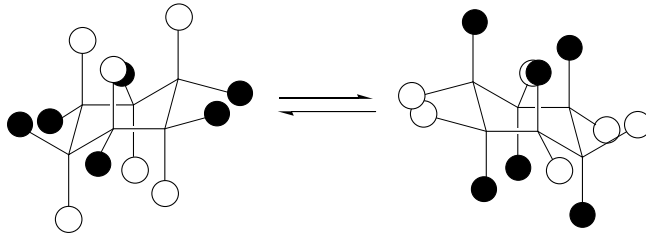## The Shape of Cyclohexane
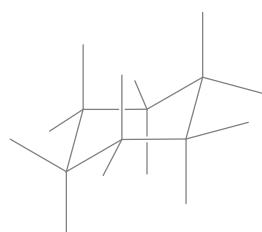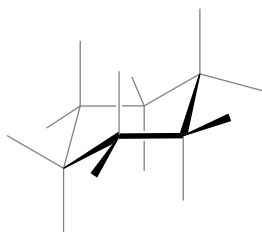
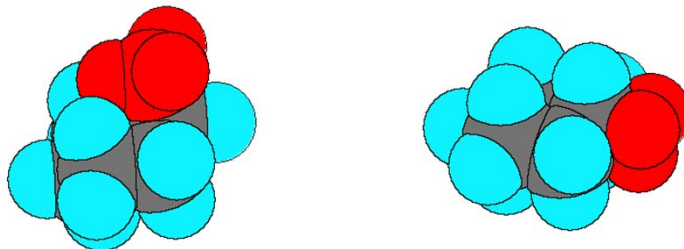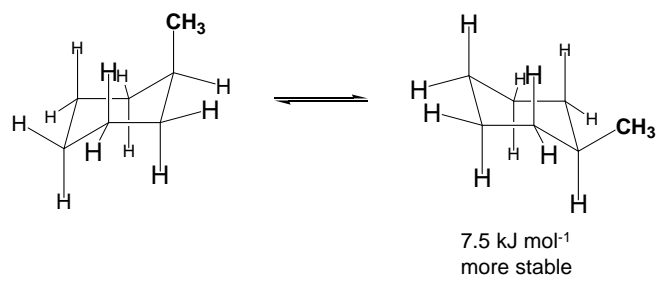## *cis* and *trans* Stereoisomers

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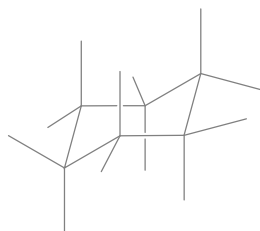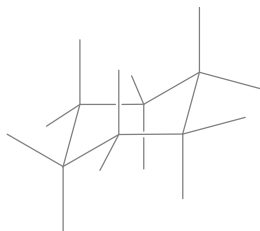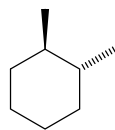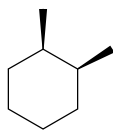
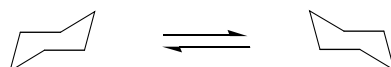*Problem:* Draw chair conformations of the following
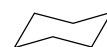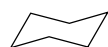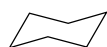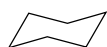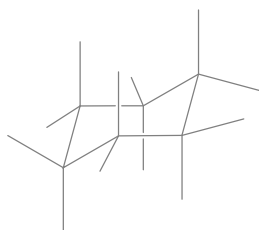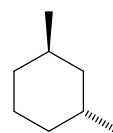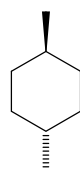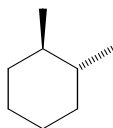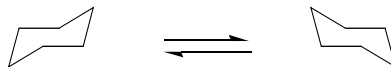
Cyclohexane Ring Inversion ("Ring Flip")

Conformational Preferences of Substituted Cyclohexanes

7.5 kJ mol^{-1}
more stable

Conformational Preferences of Disubstituted Cyclohexanes:
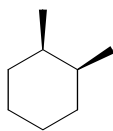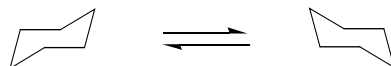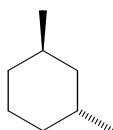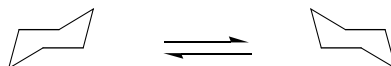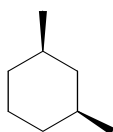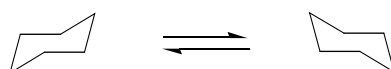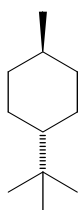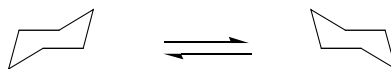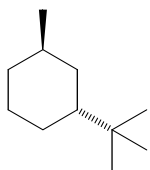
1,2-Dimethylcyclohexanes

1,3-Dimethylcyclohexanes

Conformational Preferences of Disubstituted Cyclohexanes Bearing Different Substituent

e.g.,

Larger substituents have a stronger preference for the equatorial position

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FREE-RADICAL HALOGENATION
OF ALKANES

Overall Reaction

Alkane + Halogen $\longrightarrow$ Alkyl Halide + Hydrogen Halide

Reaction is selective for substitution of hydrogen atoms on 3° over those on 1° and 2° positions.

e.g.,

$$\xrightarrow[h\nu]{Br_2}$$

$$R\text{-}H + F_2 \longrightarrow \text{BOOM!}$$

$$R\text{-}H + I_2 \longrightarrow$$
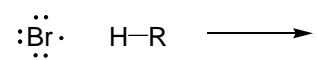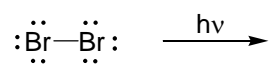
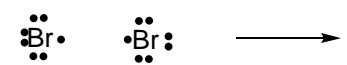http://www.duke.edu/vertices/update/win95/snail.gif89
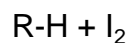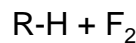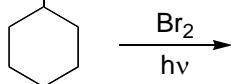
Bromination is more selective than chlorination.

Mechanism

Step 1: Initiation - generation of radicals

:Br—Br: $\xrightarrow{\text{h}\nu}$

:Br·   H—R $\longrightarrow$

Step 2: Propagation - formation of product and regeneration of radicals

:Br—Br: ·R $\longrightarrow$

Step 3: Termination - consumption of radicals

$$-\overset{|}{\underset{|}{C}}\cdot \quad \cdot\overset{|}{\underset{|}{C}}- \quad \longrightarrow$$

$$-\overset{|}{\underset{|}{C}}\cdot \quad \cdot\ddot{\underset{..}{Br}}\colon \quad \longrightarrow$$

$$\colon\ddot{\underset{..}{Br}}\cdot \quad \cdot\ddot{\underset{..}{Br}}\colon \quad \longrightarrow$$
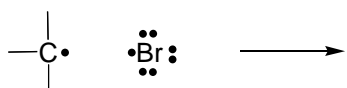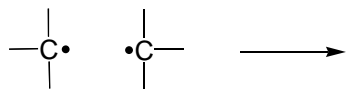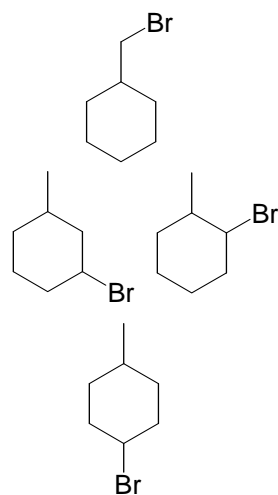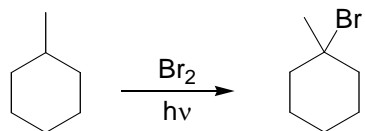
Regioselectivity

Radical bromination of alkanes is only useful when replacing a
hydrogen on a 3° carbon. Otherwise the reaction is unselective...
e.g.,

...or when there is only one possible monobrominated product.
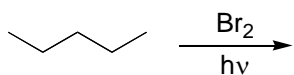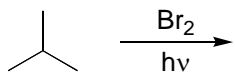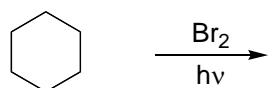*e.g.,*

Origin of Regioselectivity

Bond Dissociation Energies (R-H → R· + H·)

	$CH_3{-}H$	$CH_3CH_2{-}H$	$(CH_3)_2CH{-}H$	$(CH_3)_3C{-}H$
kJ/mol	435	410	395	381

Radical (R·) stability

$$\overset{\bullet}{C}H_3 \quad < \quad CH_3\overset{\bullet}{C}H_2 \quad < \quad (CH_3)_2\overset{\bullet}{C}H \quad < \quad (CH_3)_3\overset{\bullet}{C}$$
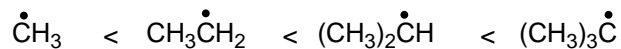
SYNTHESES OF ALKANES

Hydrogenation of Alkenes and Alkynes

$$\underset{\displaystyle /}{\overset{\displaystyle \backslash}{C}} = \underset{\displaystyle \backslash}{\overset{\displaystyle /}{C}} \qquad \xrightarrow[\text{Pt or Pd}]{H_2}$$

$$-C \equiv C- \qquad \xrightarrow[\text{Pt or Pd}]{H_2}$$
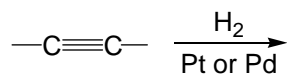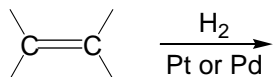
Hydrogenation is stereospecific

$$\xrightarrow[\text{Pt or Pd}]{H_2}$$

CH$_3$

CH$_3$
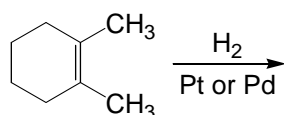
TOPIC 3

Types of Questions
- Describe structure and bonding in alkanes, alkenes, alkynes and cycloalkenes.
- Provide systematic names for hydrocarbons
- Analyze conformational preferences of alkanes and substituted cyclohexanes.
- Describe reactions of alkenes.