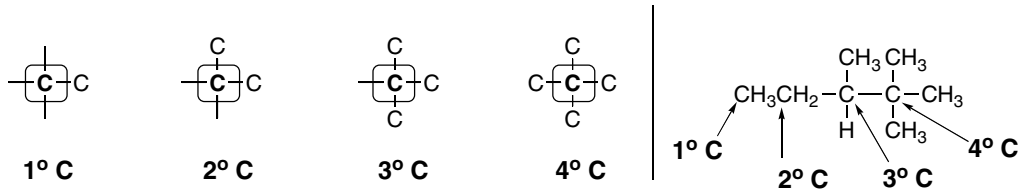
Chapter 4: Alkanes

♦ General facts about alkanes (4.1–4.3)

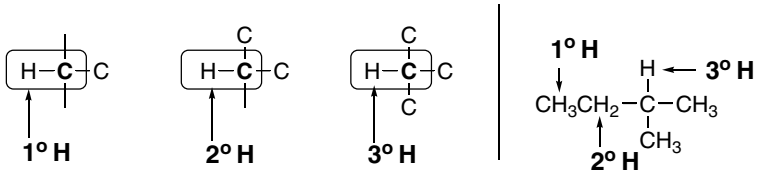
- Alkanes are composed of **tetrahedral, sp^3** hybridized C's.
- There are two types of alkanes: acyclic alkanes having molecular formula $\mathbf{C_nH_{2n+2}}$, and cycloalkanes having molecular formula $\mathbf{C_nH_{2n}}$.
- Alkanes have only **nonpolar C–C and C–H bonds** and no functional group so they undergo few reactions.
- Alkanes are named with the suffix ***-ane*.**

♦ Classifying C's and H's (4.1A)

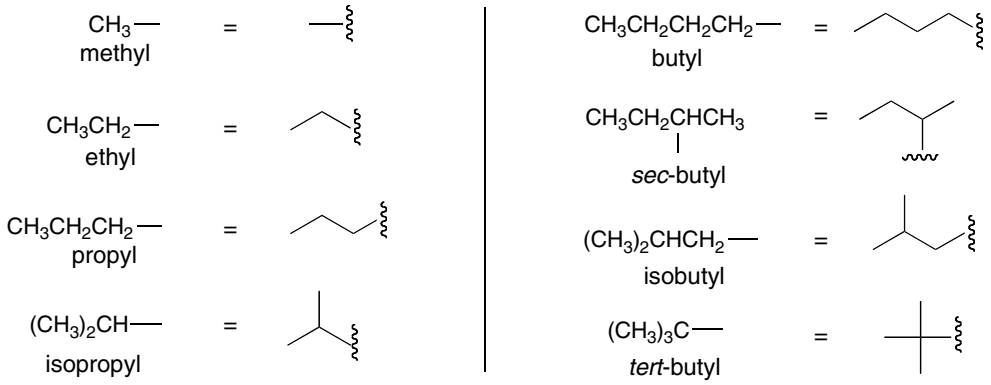
- Carbon atoms are classified by the number of C's bonded to them; **a 1° C is bonded to one other C**, and so forth.



- Hydrogen atoms are classified by the type of carbon atom to which they are bonded; **a 1° H is bonded to a 1° C,** and so forth.

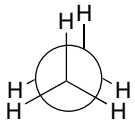
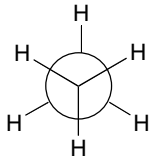
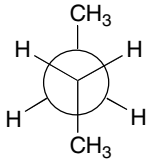
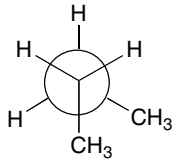


♦ Names of alkyl groups (4.4A)



♦ Conformations in acyclic alkanes (4.9, 4.10)

- Alkane conformations can be classified as **staggered**, **eclipsed**, **anti,** or **gauche** depending on the relative orientation of the groups on adjacent carbons.

eclipsed	**staggered**	**anti**	**gauche**
			
• Dihedral angle = 0°	• Dihedral angle = 60°	• Dihedral angle of 2 CH_3's = 180°	• Dihedral angle of 2 CH_3's = 60°

- A staggered conformation is **lower in energy** than an eclipsed conformation.
- An anti conformation is **lower in energy** than a gauche conformation.

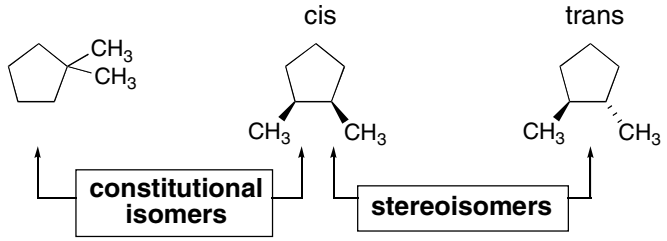
♦ Types of strain

- **Torsional strain**—an increase in energy due to eclipsing interactions (4.9).
- **Steric strain**—an increase in energy when atoms are forced too close to each other (4.10).
- **Angle strain**—an increase in energy when tetrahedral bond angles deviate from 109.5° (4.11).

♦ Two types of isomers

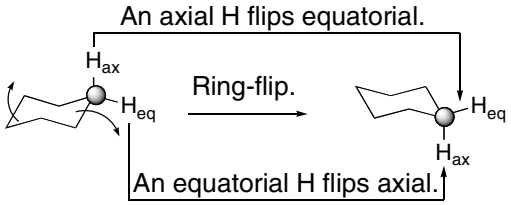
[1] **Constitutional isomers**—isomers that differ in the way the atoms are connected to each other (4.1A).

[2] **Stereoisomers**—isomers that differ only in the way atoms are oriented in space (4.13B).

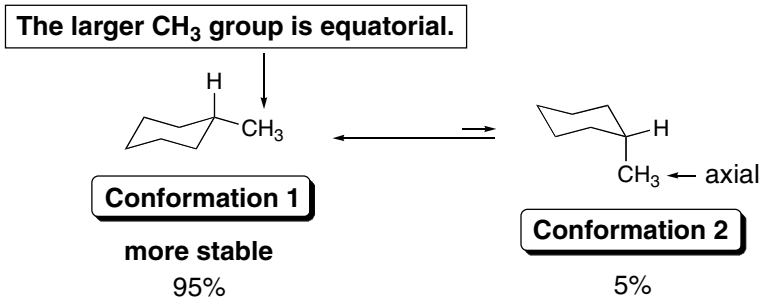


♦ Conformations in cyclohexane (4.12, 4.13)

- Cyclohexane exists as **two chair conformations** in rapid equilibrium at room temperature.
- Each carbon atom on a cyclohexane ring has **one axial** and **one equatorial hydrogen**. Ring-flipping converts axial to equatorial H's, and vice versa.



- In substituted cyclohexanes, groups larger than hydrogen are more stable in the **more roomy equatorial position.**

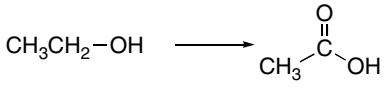


- Disubstituted cyclohexanes with substituents on different atoms exist as two possible stereoisomers.
  - The **cis** isomer has two groups on the **same side** of the ring, either both up or both down.
  - The **trans** isomer has two groups on **opposite sides** of the ring, one up and one down.

trans isomer **cis** isomer

♦ Oxidation–reduction reactions (4.14)

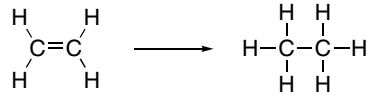
- **Oxidation** results in an **increase in the number of C–Z bonds** or a **decrease in the number of C–H bonds.**



ethanol acetic acid

Increase in C–O bonds = **oxidation**

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



ethylene ethane

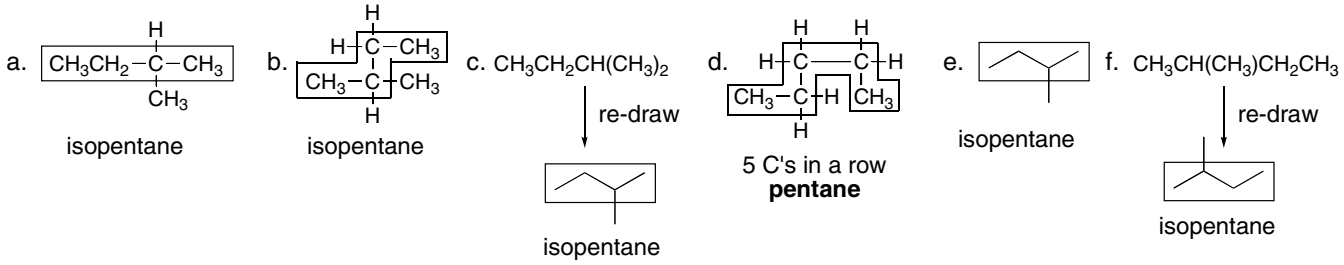
Increase in C–H bonds = **reduction**

Chapter 4: Answers to Problems

4.1 The general molecular formula for an acyclic alkane is $\mathbf{C_nH_{2n+2}}$.

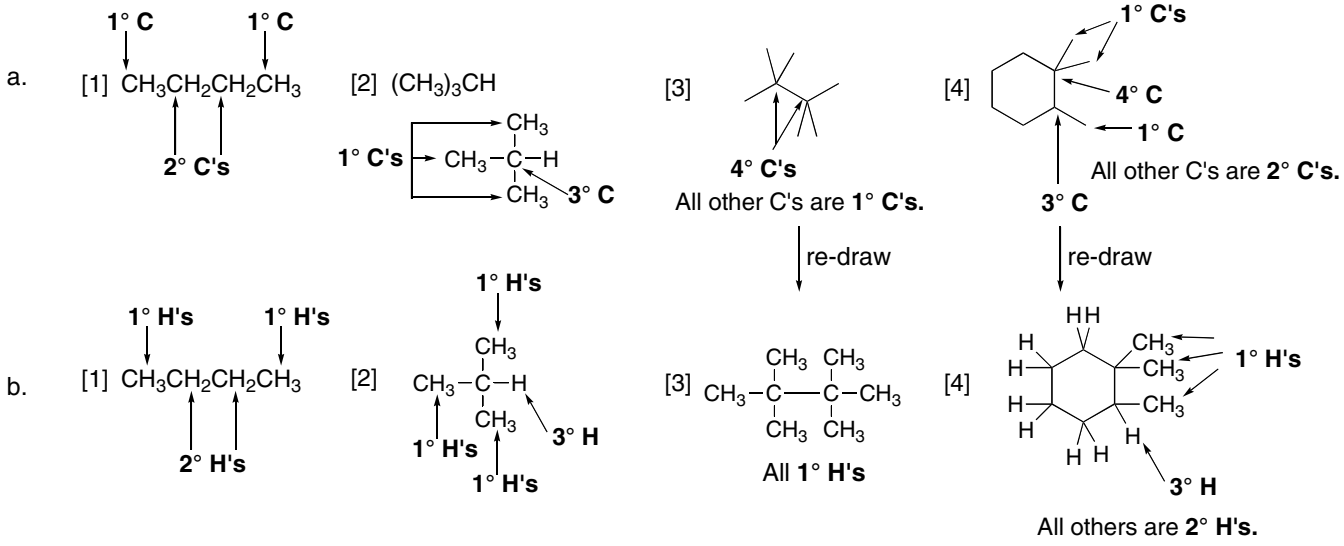
Number of C atoms = *n*	**2*n* + 2**	Number of H atoms
23	2(23) + 2 =	48
25	2(25) + 2 =	52
27	2(27) + 2 =	56

4.2 Isopentane has 4 C's in a row with a 1 C branch.

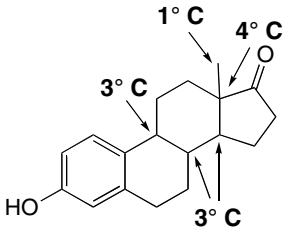


4.3 To classify a carbon atom as 1°, 2°, 3°, or 4° **determine how many carbon atoms it is bonded to** (**1° C** = bonded to **one** other C, **2° C** = bonded to **two** other C's, **3° C** = bonded to **three** other C's, **4° C** = bonded to **four** other C's). Re-draw if necessary to see each carbon clearly.

To classify a hydrogen atom as 1°, 2°, or 3°, **determine if it is bonded to a 1°, 2°, or 3° C (A 1° H is bonded to a 1° C; a 2° H is bonded to a 2° C**; **a 3° H is bonded to a 3° C).** Re-draw if necessary.



4.4 Use the definition of 1°, 2°, 3°, or 4° carbon atoms from Answer 4.3.



All other tetrahedral C's are **2° C's.**

4.5 Constitutional isomers differ in the way the atoms are connected to each other. To draw all the constitutional isomers:

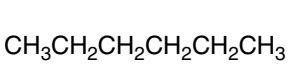
[1] Draw all of the C's in a long chain.

[2] Take off one C and use it as a substituent. (Don't add it to the end carbon: this re-makes the long chain.)

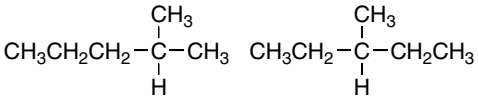
[3] Take off two C's and use these as substituents, etc.

Five **constitutional isomers** of molecular formula C_6H_{14}:

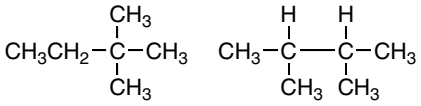
[1] long chain



[2] with one C as a substituent

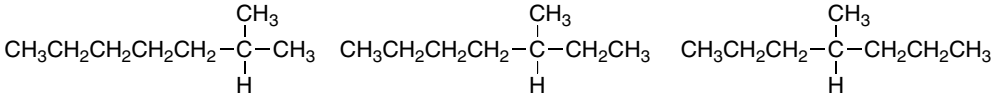


[3] using two C's as substituents

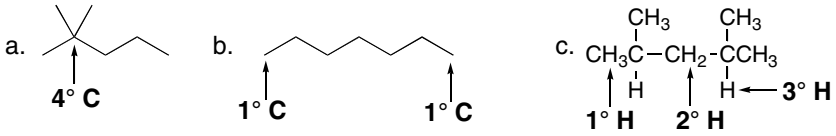


4.6

Molecular formula C_8H_{18} with one CH_3 substituent:

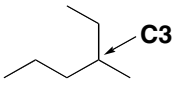


4.7 Draw each alkane to satisfy the requirements.



All other C's are **2° C's**.

4.8 Draw each compound as a skeletal structure to compare the compounds.

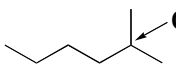


A

CH_3 bonded to C3

identical to compound **C**

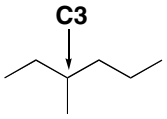
$CH_3(CH_2)_3CH(CH_3)_2$ =



B

CH_3 bonded to C2

$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$ =



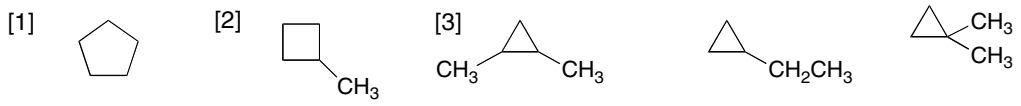
C

CH_3 bonded to C3

identical to compound **A**

4.9 Use the steps from Answer 4.5 to draw the constitutional isomers.

Five **constitutional isomers** of molecular formula C_5H_{10} having one ring:

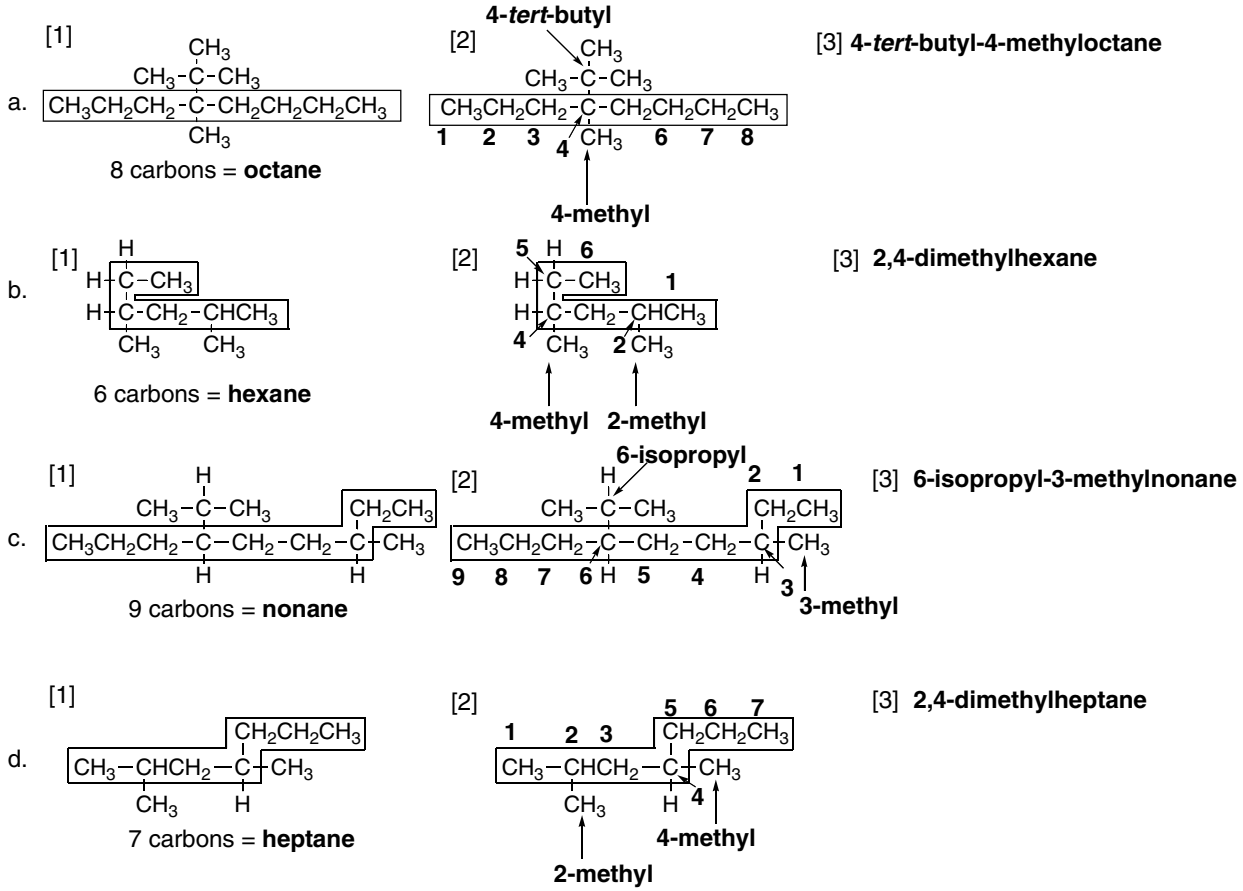


4.10 Follow these steps to name an alkane:

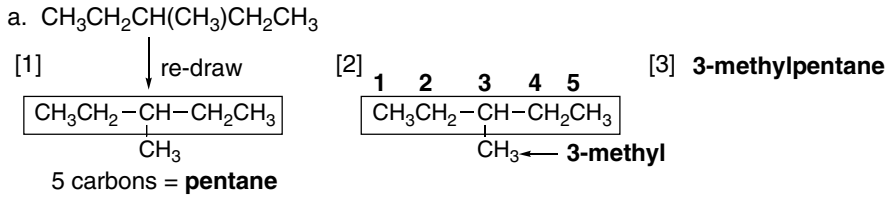
[1] **Name the parent chain** by finding the longest C chain.

[2] **Number the chain** so that the first substituent gets the lower number. Then **name and number all substituents**, giving like substituents a prefix (di, tri, etc.).

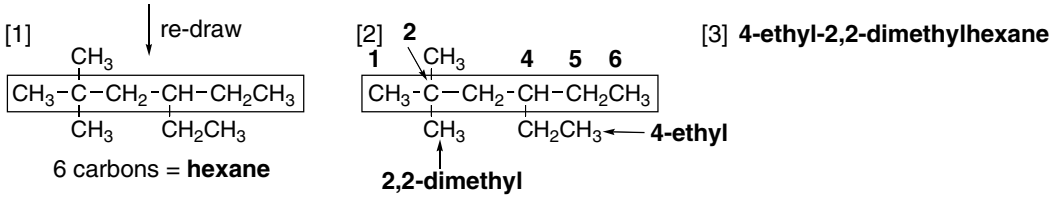
[3] **Combine all parts**, alphabetizing the substituents, ignoring all prefixes except *iso*.



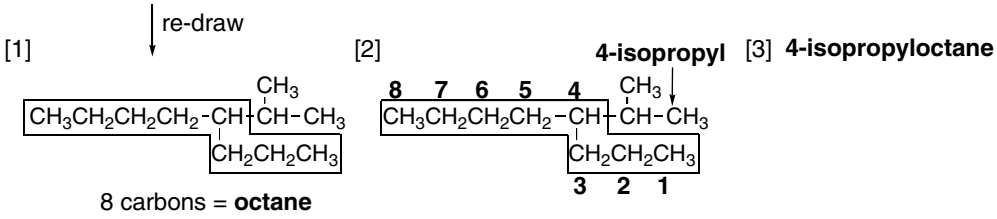
4.11 Use the steps in Answer 4.10 to name each alkane.



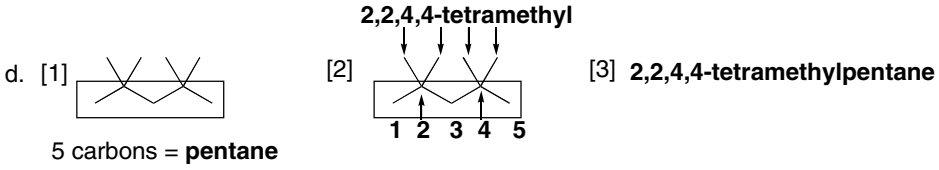
b. $(CH_3)_3CCH_2CH(CH_2CH_3)_2$



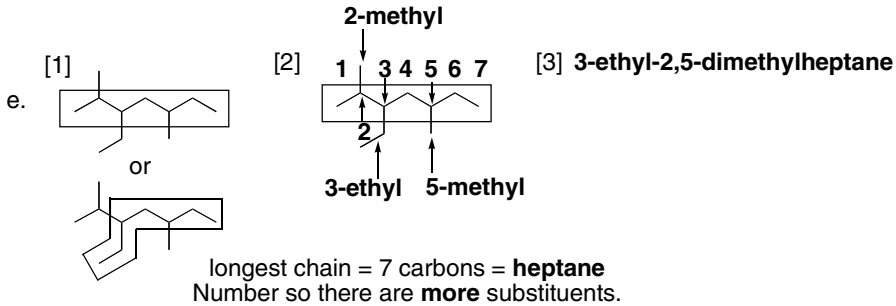
c. $CH_3(CH_2)_3CH(CH_2CH_2CH_3)CH(CH_3)_2$



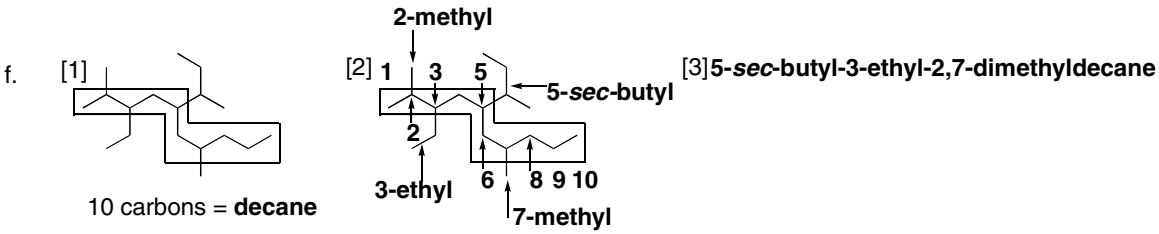
d.



e.



f.



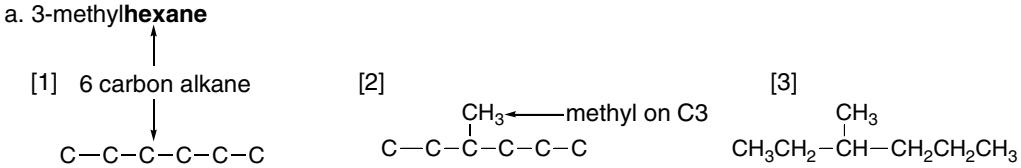
4.12 To work backwards from a name to a structure:

[1] Find the parent name and draw that number of C's. Use the suffix to identify the functional group **(-ane = alkane)**.

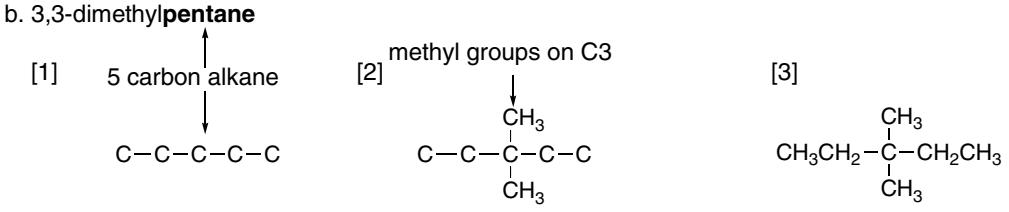
[2] Arbitrarily number the C's in the chain. Add the substituents to the appropriate C's.

[3] Re-draw with H's to make C's have four bonds.

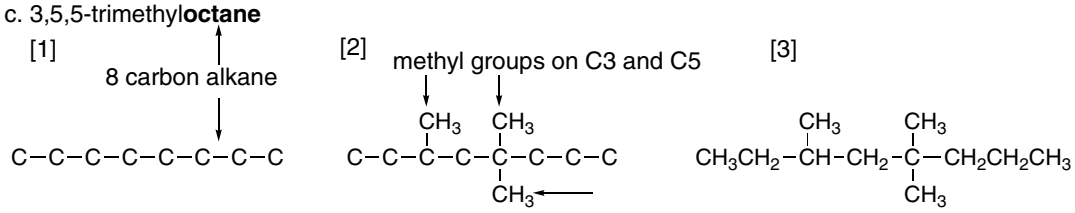
a. 3-methyl**hexane**



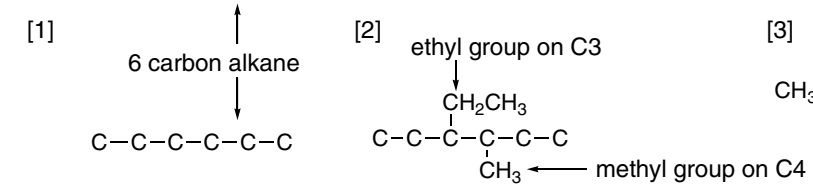
b. 3,3-dimethyl**pentane**



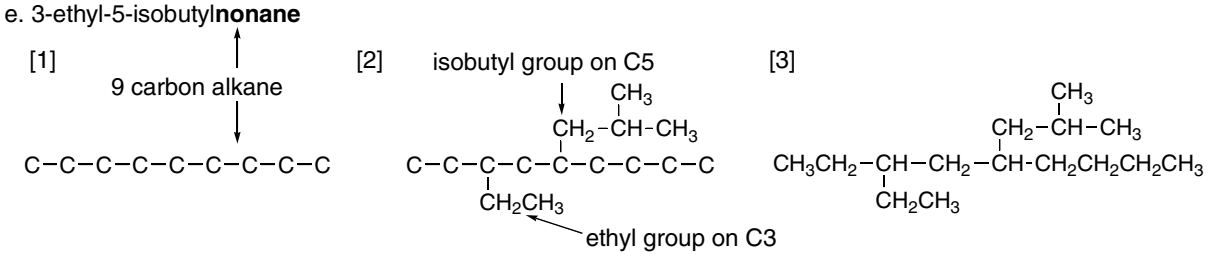
c. 3,5,5-trimethyl**octane**



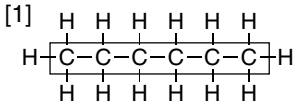
d. 3-ethyl-4-methyl**hexane**



e. 3-ethyl-5-isobutyl**nonane**

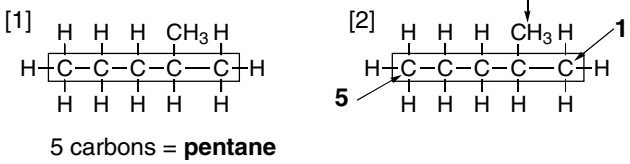


4.13 Use the steps in Answer 4.10 to name each alkane.

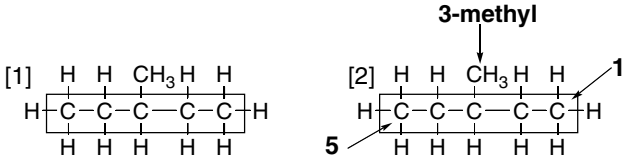


[2] no substituents, skip [2]

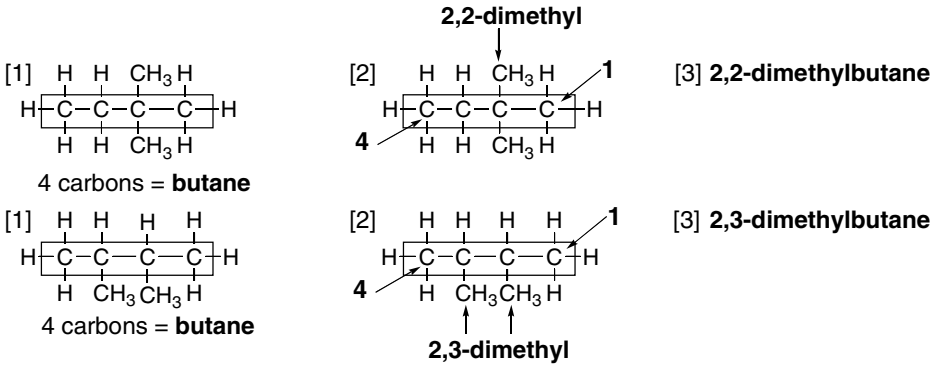
[3] **hexane**



[3] **2-methylpentane**



[3] **3-methylpentane**



4.14 Follow these steps to name a cycloalkane:

[1] **Name the parent cycloalkane** by counting the C's in the ring and adding cyclo-.

[2] **Numbering:**

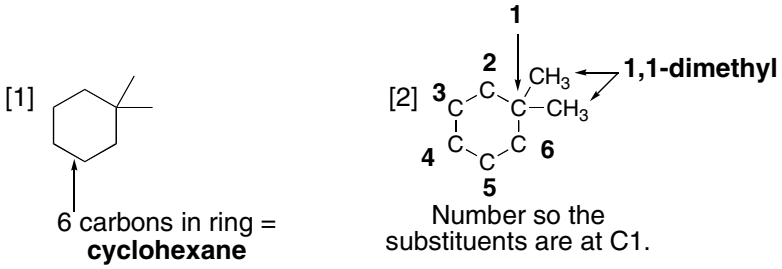
[2a] Number around the ring beginning at a substituent and giving the second substituent the lower number.

[2b] Number to assign the lower number to the substituents alphabetically.

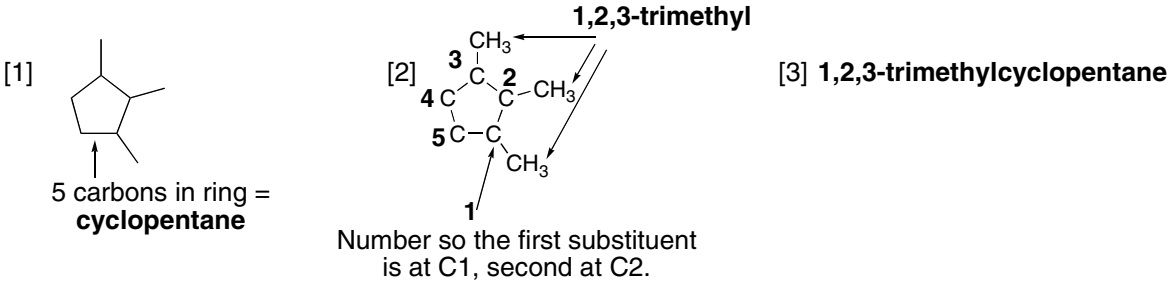
[2c] Name and number all substituents, giving like substituents a prefix (di, tri, etc.).

[3] **Combine all parts**, alphabetizing the substituents, ignoring all prefixes except *iso*. (Remember: If a carbon chain has more C's than the ring, the chain is the parent, and the ring is a substituent.)

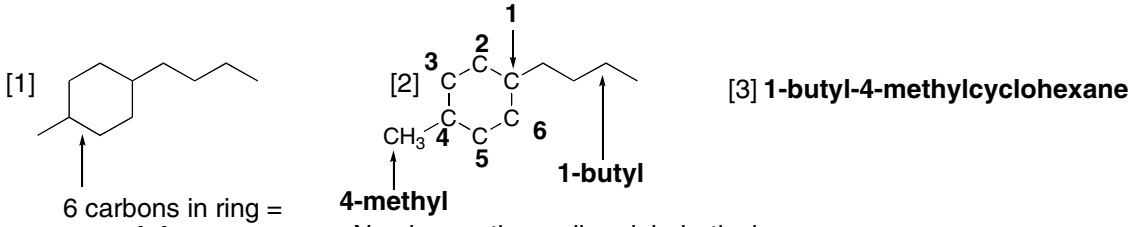
a.



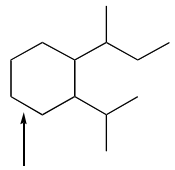
b.



c.

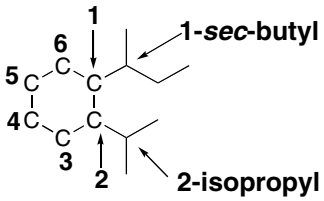


d. [1]



6 carbons in ring = **cyclohexane**

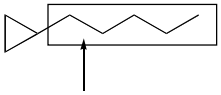
[2]



Number so the earlier alphabetical substituent is at C1, **b**utyl before **i**sopropyl.

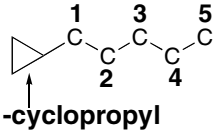
[3] **1-*sec*-butyl-2-isopropylcyclohexane**

e. [1]



longest chain = 5 carbons = **pentane**

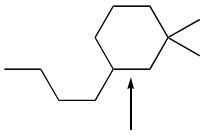
[2]



Number so the cyclopropyl is at C1.

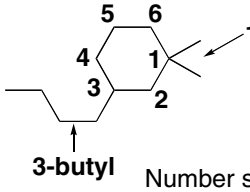
[3] **1-cyclopropylpentane**

f. [1]



6 carbons in ring = **cyclohexane**

[2]



Number so the two methyls are at C1.

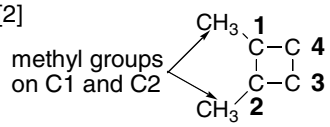
[3] **3-butyl-1,1-dimethylcyclohexane**

4.15 To draw the structures, use the steps in Answer 4.12.

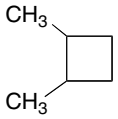
a. 1,2-dimethyl**cyclobutane**

[1] 4 carbon cycloalkane

[2]



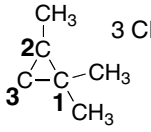
[3]



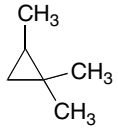
b. 1,1,2-trimethyl**cyclopropane**

[1] 3 carbon cycloalkane

[2]

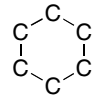


[3]

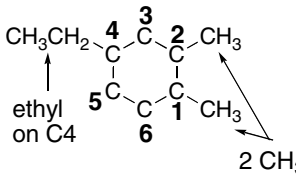


c. 4-ethyl-1,2-dimethyl**cyclohexane**

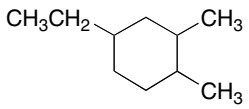
[1] 6 carbon cycloalkane



[2]



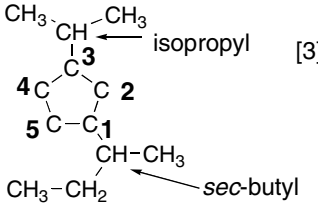
[3]



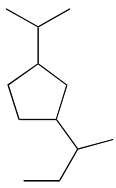
d. 1-*sec*-butyl-3-isopropyl**cyclopentane**

[1] 5 carbon cycloalkane

[2]

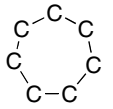


[3]

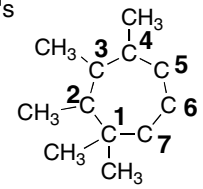


e. 1,1,2,3,4-pentamethyl**cycloheptane**

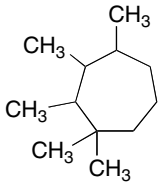
[1] 7 carbon cycloalkane



[2] 5 CH_3's

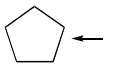


[3]



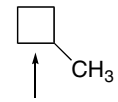
4.16 To name the cycloalkanes, use the steps from Answer 4.14.

[1]



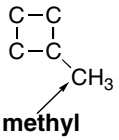
5 carbons in ring = **cyclopentane**

[1]



4 carbons in ring = **cyclobutane**

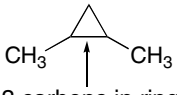
[2]



methyl

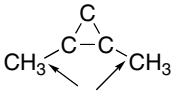
[3] **methylcyclobutane**

[1]



3 carbons in ring = **cyclopropane**

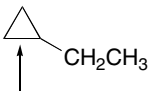
[2]



1,2-dimethyl

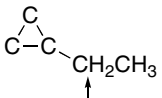
[3] **1,2-dimethylcyclopropane**

[1]



3 carbons in ring = **cyclopropane**

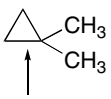
[2]



ethyl

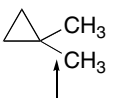
[3] **ethylcyclopropane**

[1]



3 carbons in ring = **cyclopropane**

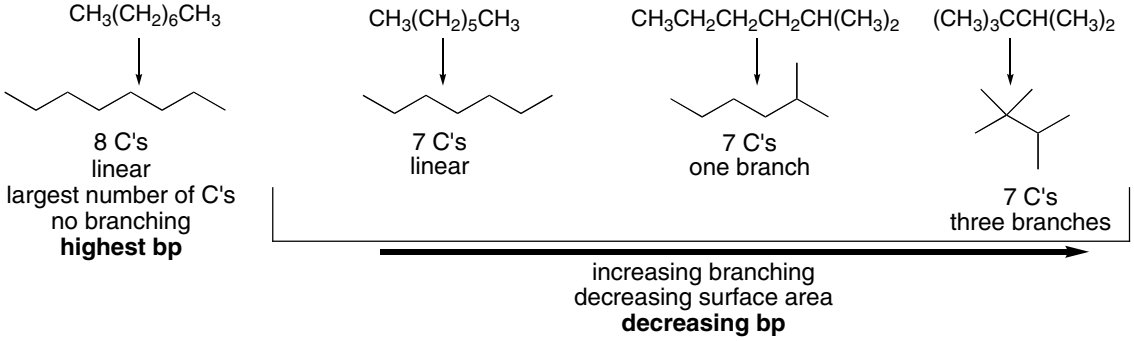
[2]



1,1-dimethyl

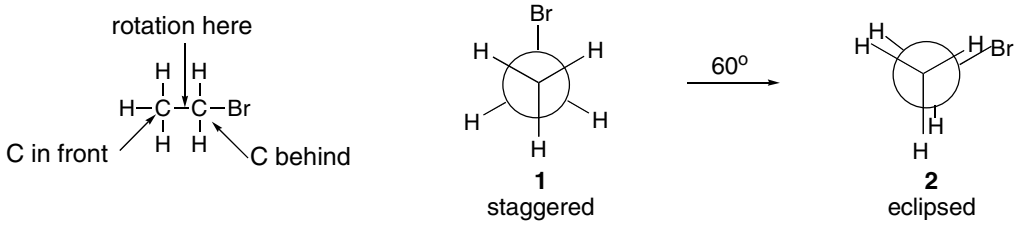
[3] **1,1-dimethylcyclopropane**

4.17 Compare the number of C's and surface area to determine relative boiling points. Rules:
[1] Increasing number of C's = increasing boiling point.
[2] Increasing surface area = increasing boiling point (branching decreases surface area).

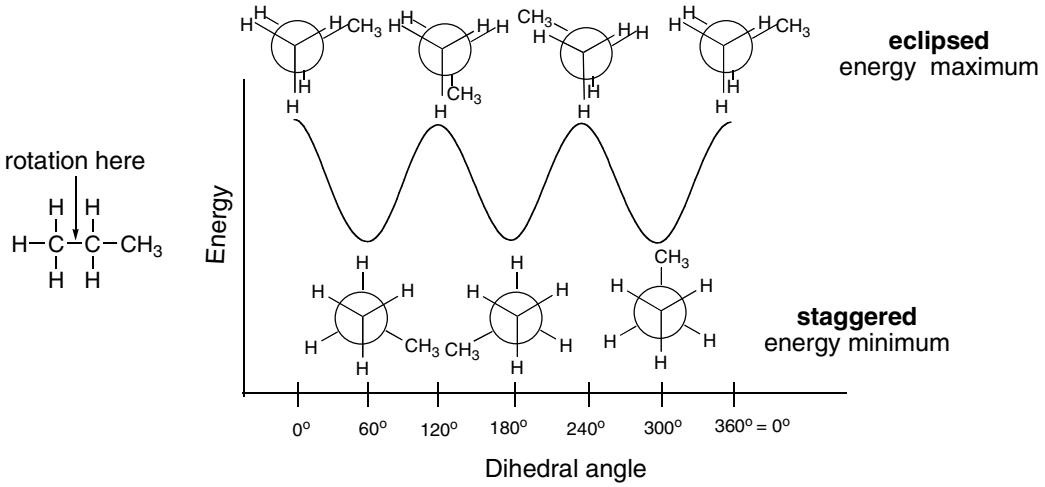


Increasing boiling point: $(CH_3)_3CCH(CH_3)_2 < CH_3CH_2CH_2CH_2CH(CH_3)_2 < CH_3(CH_2)_5CH_3 < CH_3(CH_2)_6CH_3$

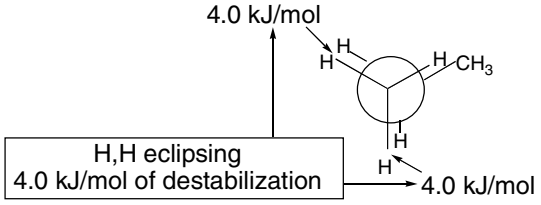
4.18 To draw a Newman projection, visualize the carbons as one in front and one in back of each other. The C–C bond is not drawn. There is only one staggered and one eclipsed conformation.



4.19 Staggered conformations are more stable than eclipsed conformations.



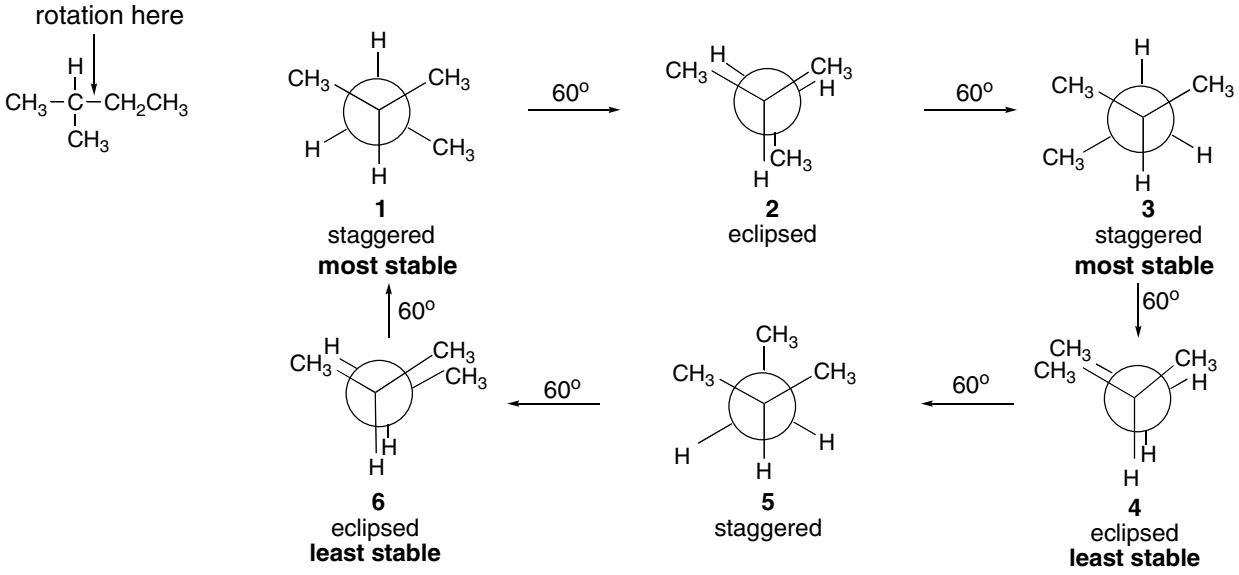
4.20



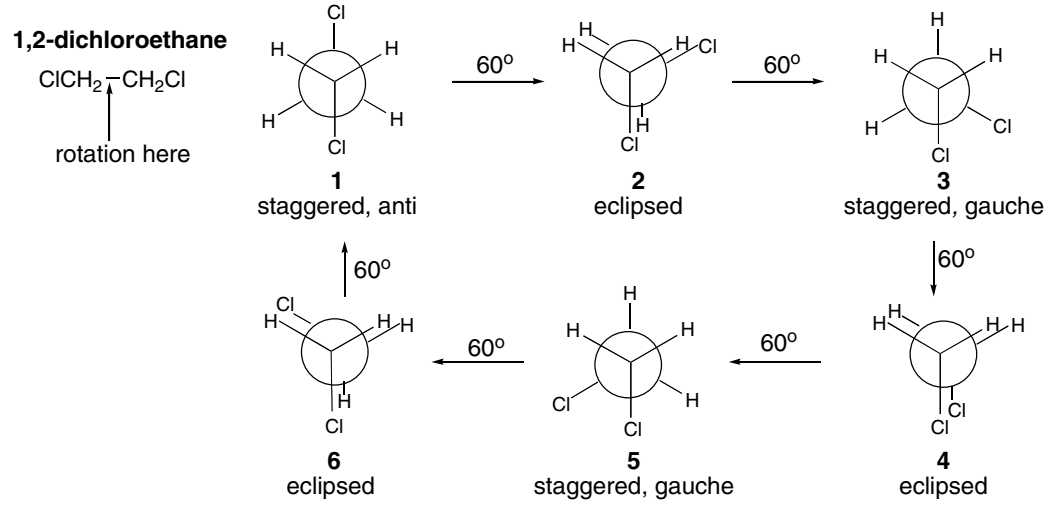
To calculate H,CH_3 destabilization:

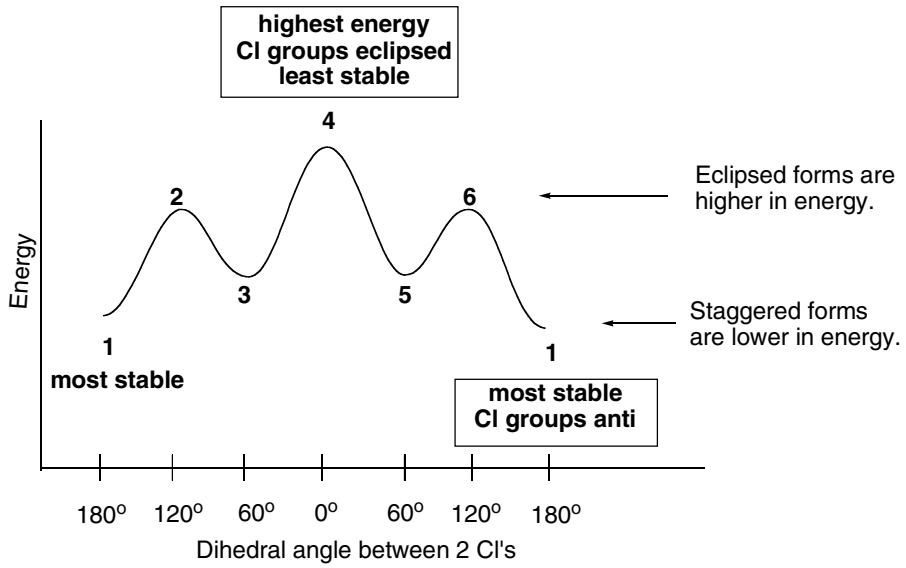
14 kJ/mol (total) –
8.0 kJ/mol for 2 H,H eclipsing interactions
= **6 kJ/mol** for one H,CH_3 eclipsing interaction

4.21 To determine the energy of conformations keep two things in mind:
[1] Staggered conformations are more stable than eclipsed conformations.
[2] Minimize steric interactions: keep large groups away from each other.
The highest energy conformation is the eclipsed conformation in which the two largest groups are eclipsed. The lowest energy conformation is the staggered conformation in which the two largest groups are anti.

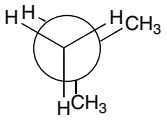


4.22 To determine the most and least stable conformations, use the rules from Answer 4.21.

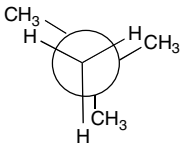




4.23 Add the energy increase for each eclipsing interaction to determine the destabilization.

a. 

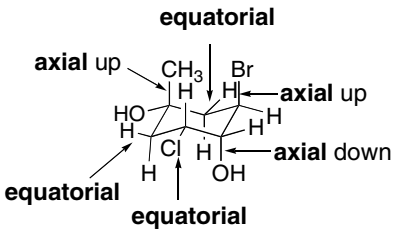
1 H,H interaction =	4.0 kJ/mol
2 H,CH_3 interactions (2 x 6.0 kJ/mol) =	12.0 kJ/mol
Total destabilization =	**16 kJ/mol**

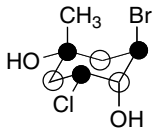
b. 

3 H,CH_3 interactions
(3 x 6.0 kJ/mol) = **18 kJ/mol**

Total destabilization

4.24 Two points:
- Axial bonds point up or down, while equatorial bonds point out.
- An *up* carbon has an axial *up* bond, and a *down* carbon has an axial *down* bond.

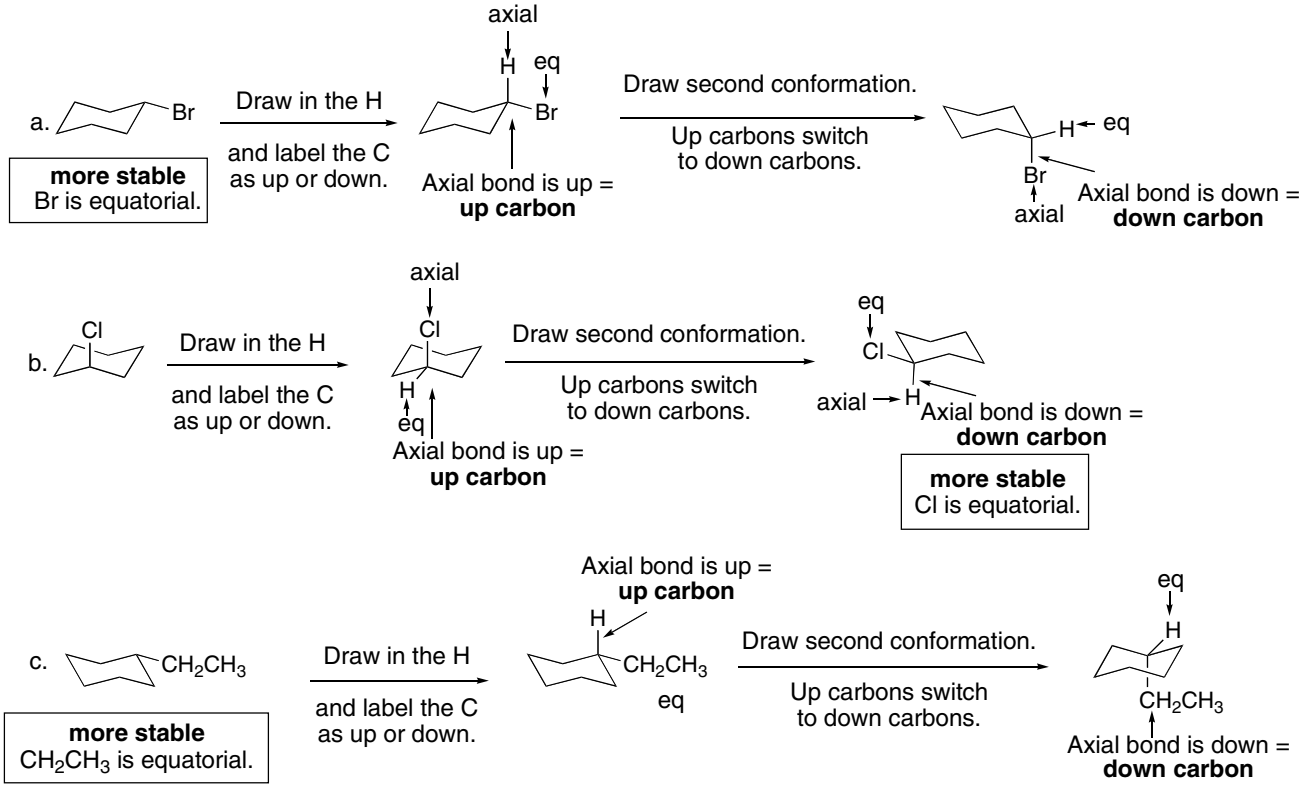




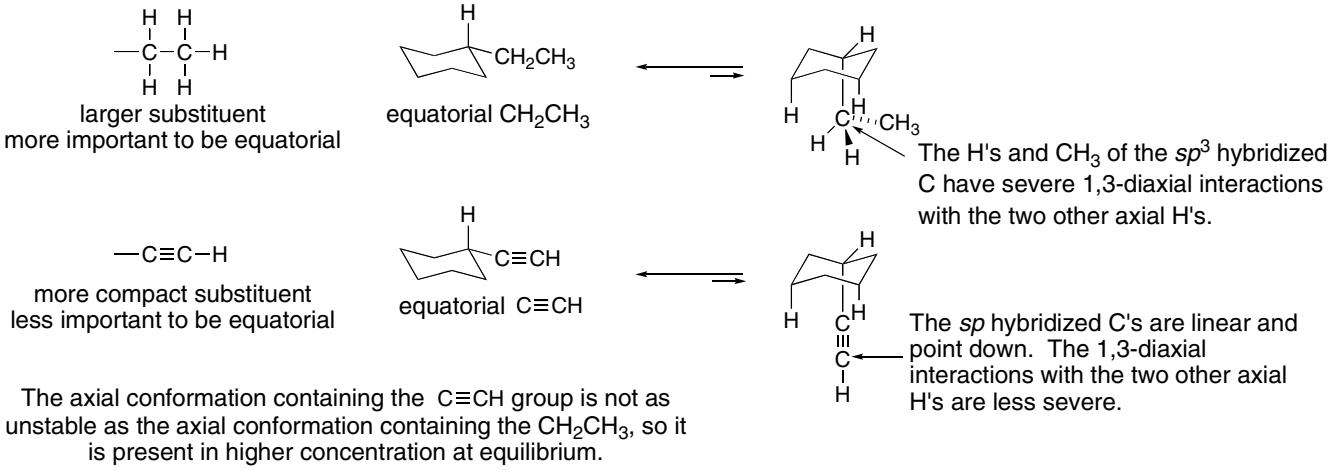
Up carbons are dark circles.
Down carbons are clear circles.

4.25 Draw the second chair conformation by flipping the ring**.**

- **The *up* carbons become *down* carbons, and the axial bonds become equatorial bonds.**
- **Axial bonds become equatorial, but *up* bonds stay *up***; i.e., an axial *up* bond becomes an equatorial *up* bond.
- The conformation with **larger groups equatorial is the more stable** conformation and is present in higher concentration at equilibrium.



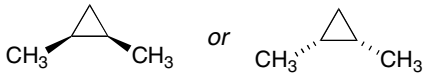
4.26 Larger axial substituents create unfavorable diaxial interactions, whereas equatorial groups have more room and are favored.



The axial conformation containing the C≡CH group is not as unstable as the axial conformation containing the CH_2CH_3, so it is present in higher concentration at equilibrium.

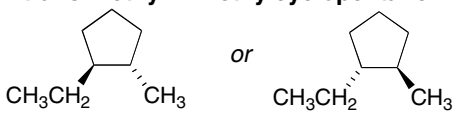
4.27 Wedges represent "up" groups in front of the page, and dashes are "down" groups in back of the page. Cis groups are on the same side of the ring, and trans groups are on opposite sides of the ring.

a. ***cis*-1,2-dimethylcyclopropane**



cis = same side of the ring
both groups on wedges or
both on dashes

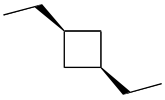
b. ***trans*-1-ethyl-2-methylcyclopentane**



trans = opposite sides of the ring
one group on a wedge,
one group on a dash

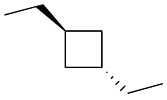
4.28 Cis and trans isomers are stereoisomers.

***cis*-1,3-diethylcyclobutane**



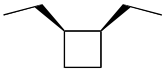
cis = same side of the ring
both groups on wedges or
both on dashes

a. ***trans*-1,3-diethylcyclobutane**



trans = opposite sides of the ring
one group on a wedge,
one group on a dash

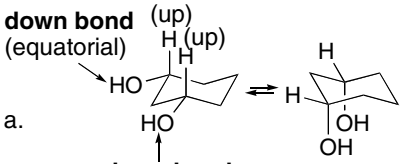
b. ***cis*-1,2-diethylcyclobutane**



constitutional isomer
different arrangement of atoms

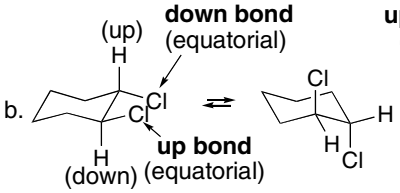
4.29 To classify a compound as a cis or trans isomer, **classify each non-hydrogen group as up or down. Groups on the same side = cis isomer, groups on opposite sides = trans isomer.**

a.



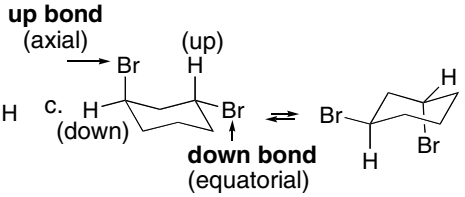
both groups down =
cis isomer

b.



one group up, one down =
trans isomer

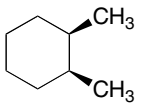
c.



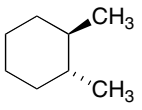
one group up, one down =
trans isomer

4.30

a.

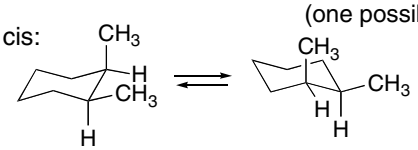


groups on same side
cis isomer



groups on opposite sides
trans isomer
(one possibility)

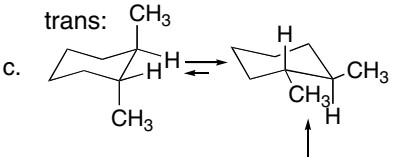
b.



two chair conformations for the **cis isomer**

Same stability since they both have
one equatorial, one axial CH_3 group.

c.

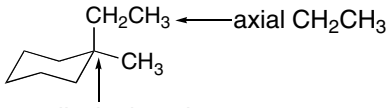


both groups equatorial
more stable

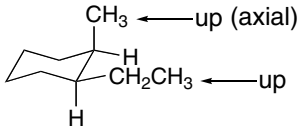
two chair conformations for the **trans isomer**

d. The **trans isomer is more stable** because it can have both methyl groups in the more roomy **equatorial** position.

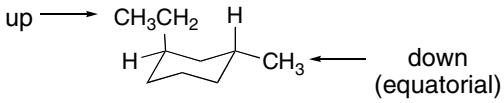
4.31

a. 

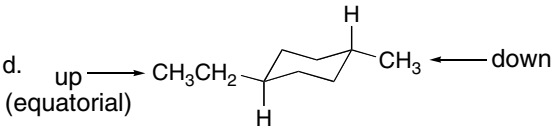
1,1-disubstituted

b. 

cis-1,2-disubstituted

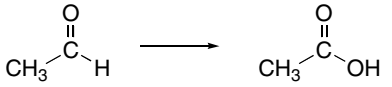
c. 

trans-1,3-disubstituted

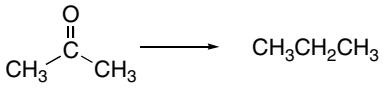
d. 

trans-1,4-disubstituted

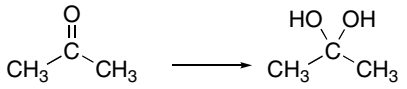
4.32 *Oxidation* results in an *increase* in the number of C–Z bonds, or a *decrease* in the number of C–H bonds.
Reduction results in a *decrease* in the number of C–Z bonds, or an *increase* in the number of C–H bonds.

a. 

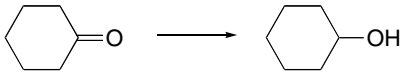
Decrease in the number of C–H bonds.
Increase in the number of C–O bonds.
Oxidation

b. 

Decrease in the number of C–O bonds.
Increase in the number of C–H bonds.
Reduction

c. 

No change in the number of C–O
or C–H bonds. **Neither**

d. 

Decrease in the number of C–O bonds.
Increase in the number of C–H bonds.
Reduction

4.33 The products of a combustion reaction of a hydrocarbon are always the same: **CO_2 and H_2O.**

a. $CH_3CH_2CH_3 + 5\ O_2 \xrightarrow{\text{flame}} 3\ CO_2 + 4\ H_2O + \text{heat}$

b.  $+ 9\ O_2 \xrightarrow{\text{flame}} 6\ CO_2 + 6\ H_2O + \text{heat}$

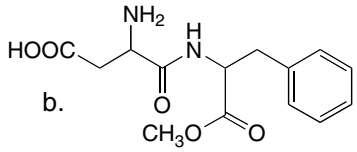
4.34 Lipids contain many nonpolar C–C and C–H bonds and few polar functional groups.

a. $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$

oleic acid

only one polar functional group
18 carbons
a lipid

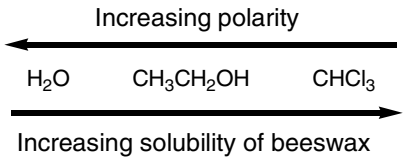
b.



aspartame

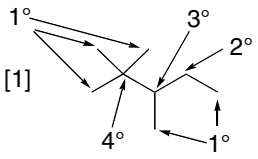
many polar functional groups
only 14 carbons
not a lipid

4.35 "Like dissolves like." Beeswax is a lipid, and therefore, it will be more soluble in nonpolar solvents. H_2O is very polar, ethanol is slightly less polar, and chloroform is least polar. Beeswax is most soluble in the least polar solvent.

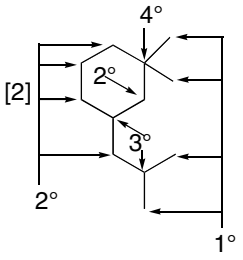


4.36 Use the rules from Answer 4.3.

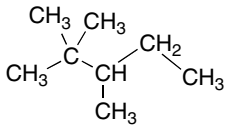
a. [1]



[2]

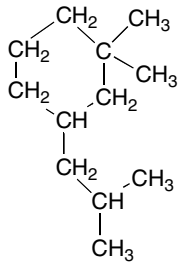


b. [1]



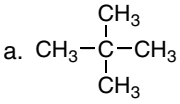
All CH_3's have 1° H's.
All CH_2's have 2° H's.
All CH's have 3° H's.

[2]



4.37

One possibility:

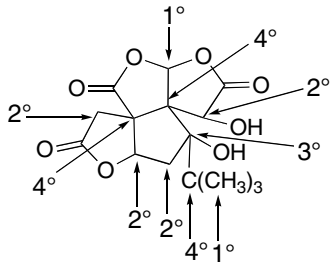
a. 

b. 

c. $CH_3CH_2CH_3$

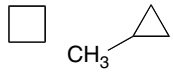
d. $(CH_3)_3CH$

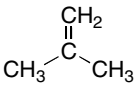
4.38 Use the rules from Answer 4.3.



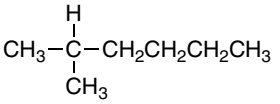
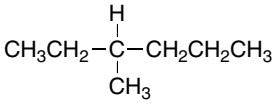
4.39

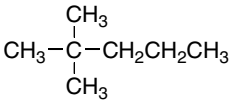
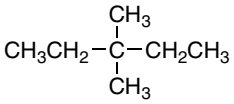
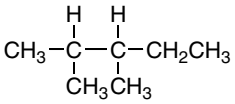
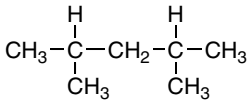
a. Five constitutional isomers of molecular formula C_4H_8:

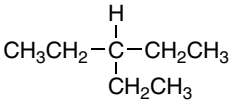
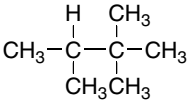


$CH_3CH{=}CHCH_3$ $CH_2{=}CHCH_2CH_3$ 

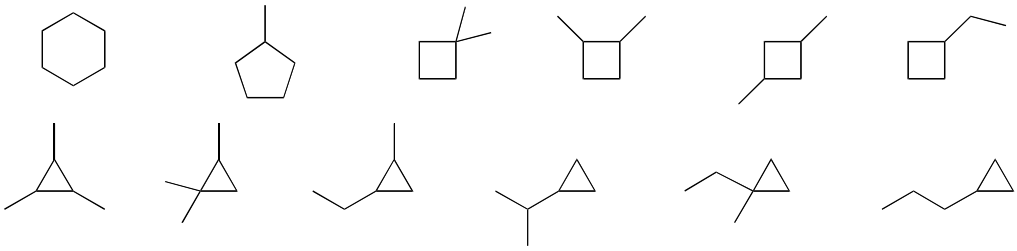
b. Nine constitutional isomers of molecular formula C_7H_{16}:

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$  

c. Twelve constitutional isomers of molecular formula C_6H_{12} containing one ring:



4.40 Use the steps in Answers 4.10 and 4.14 to name the alkanes.

a. $CH_3CH_2CHCH_2CHCH_2CH_2CH_3$

[1] CH_3 CH_2CH_3 — 8 carbons = **octane**

[2] **1 2 3 4 5 6 7 8** $CH_3CH_2CHCH_2CHCH_2CH_2CH_3$ (CH_3 **3-methyl**, CH_2CH_3 **5-ethyl**)

[3] **5-ethyl-3-methyloctane**

b. $CH_3CH_2CCH_2CH_2CHCHCH_2CH_2CH_3$

[1] CH_2CH_3 CH_3 CH_2CH_3 CH_2CH_3 — 10 carbons = **decane**

[2] **1 2 3** CH_2CH_3, **7** CH_3 (**7-methyl**) $CH_3CH_2CCH_2CH_2CHCHCH_2CH_2CH_3$ (CH_2CH_3 CH_2CH_3 **3,3,6-triethyl**)

[3] **3,3,6-triethyl-7-methyldecane**

c. $CH_3CH_2CH_2C(CH_3)_2C(CH_3)_2CH_2CH_3$

[1] re-draw: $CH_3CH_2CH_2-C(CH_3)_2-C(CH_3)_2-CH_2CH_3$ — 7 carbons = **heptane**

[2] **3** CH_3 CH_3; **2** CH_3 CH_3; **1**; **4** — **3,3,4,4-tetramethyl**

[3] **3,3,4,4-tetramethylheptane**

d. $CH_3CH_2C(CH_2CH_3)_2CH(CH_3)CH(CH_2CH_2CH_3)_2$

[1] re-draw: $CH_3CH_2-C(CH_3CH_2)(H)-C(H)-C(CH_3CH_2)(CH_3)-CH_2CH_2CH_3$ — 8 carbons = **octane**

[2] **3,3-diethyl**; **4** CH_3CH_2 H; **5** H; **1**; CH_3CH_2 CH_3 $CH_2CH_2CH_3$ (**4-methyl**, **5-propyl**)

[3] **3,3-diethyl-4-methyl-5-propyloctane**

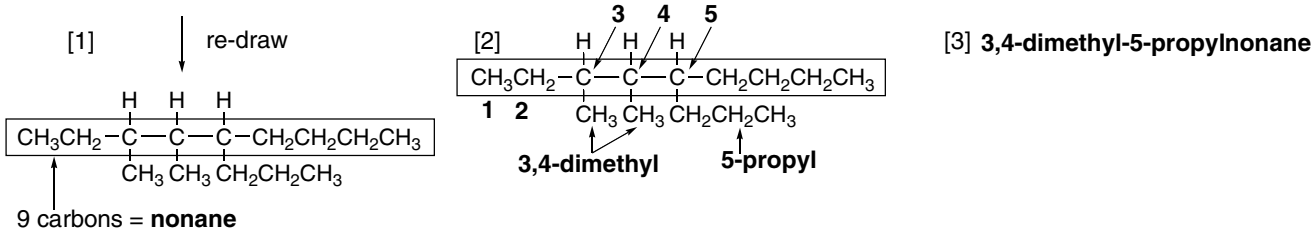
e. $(CH_3CH_2)_3CCH(CH_3)CH_2CH_2CH_3$

[1] re-draw: $CH_3CH_2-C(CH_3CH_2)(H)-C(CH_3CH_2)(CH_3)-CH_2CH_2CH_3$ — 7 carbons = **heptane**

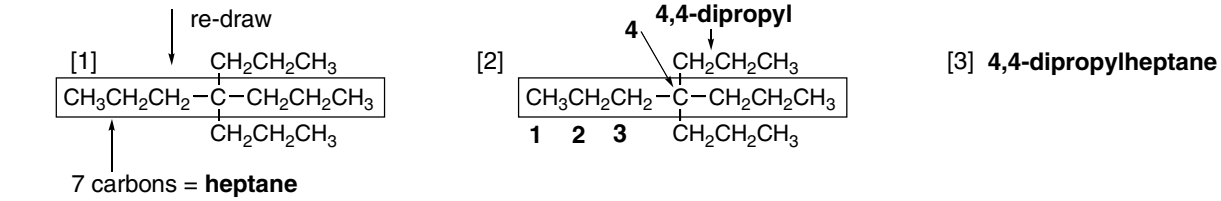
[2] **3,3-diethyl**; **4** CH_3CH_2 H; **1**; CH_3CH_2 CH_3 (**4-methyl**); **6 7**

[3] **3,3-diethyl-4-methylheptane**

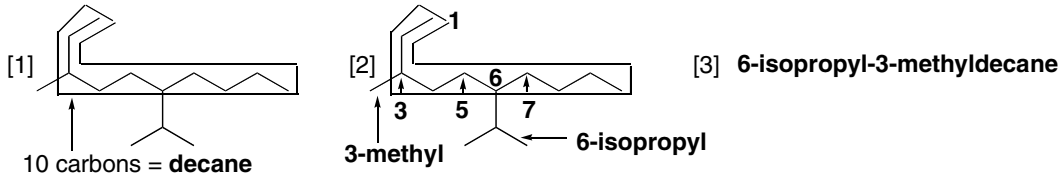
f. $CH_3CH_2CH(CH_3)CH(CH_3)CH(CH_2CH_2CH_3)(CH_2)_3CH_3$



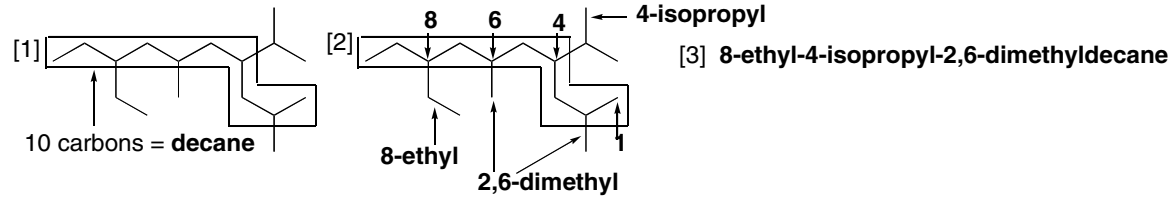
g. $(CH_3CH_2CH_2)_4C$



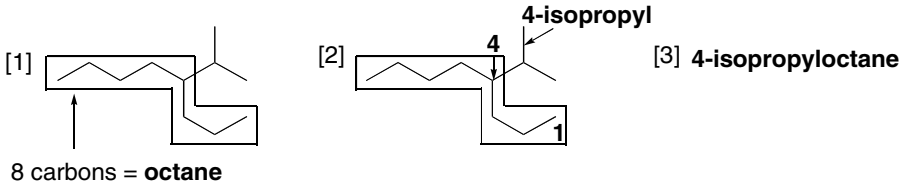
h.



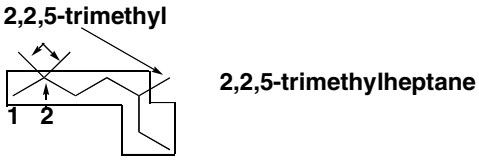
i.



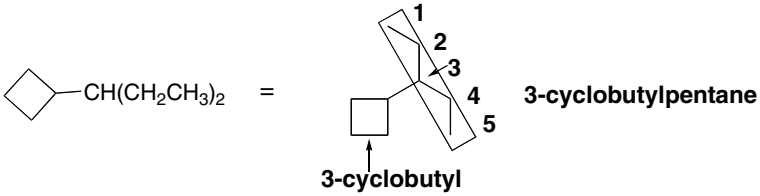
j.



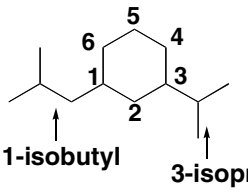
k.



l.

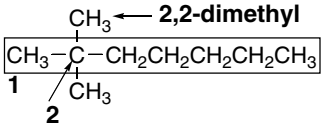


m.

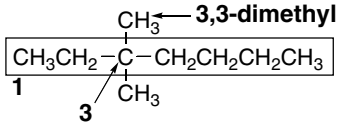
n. 

1-isobutyl-3-isopropylcyclohexane

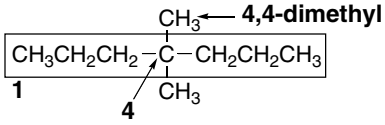
4.41



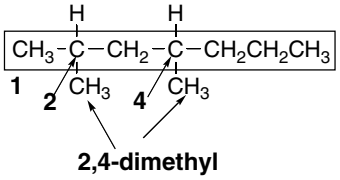
2,2-dimethylheptane



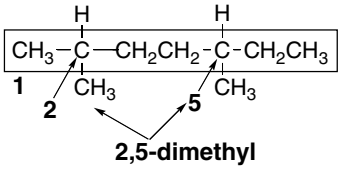
3,3-dimethylheptane



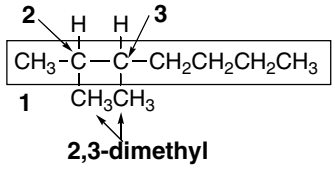
4,4-dimethylheptane



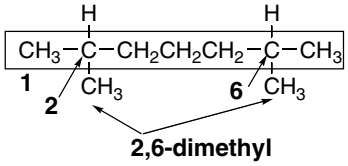
2,4-dimethylheptane



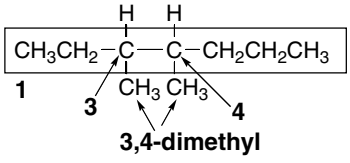
2,5-dimethylheptane



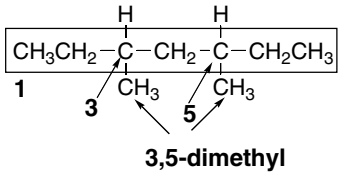
2,3-dimethylheptane



2,6-dimethylheptane



3,4-dimethylheptane

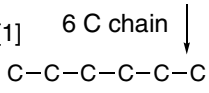


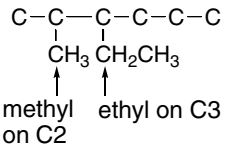
3,5-dimethylheptane

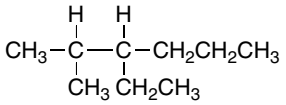
4.42 Use the steps in Answer 4.12 to draw the structures.

a. 3-ethyl-2-methyl**hexane**

[1] 6 C chain

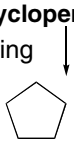


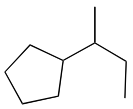
[2] 

[3] 

b. *sec*-butyl**cyclopentane**

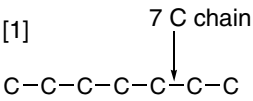
[1] 5 C ring

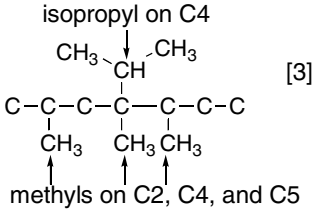


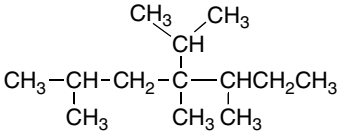
[2] 

c. 4-isopropyl-2,4,5-trimethyl**heptane**

[1] 7 C chain

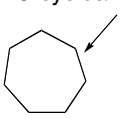


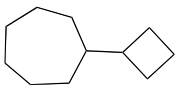
[2] 

[3] 

d. cyclobutyl**cycloheptane**

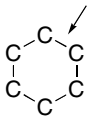
[1] 7 C cycloalkane



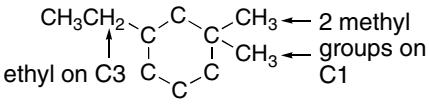
[2] 

e. 3-ethyl-1,1-dimethyl**cyclohexane**

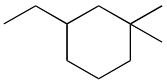
[1] 6 C cycloalkane



[2]

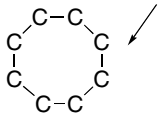


[3]

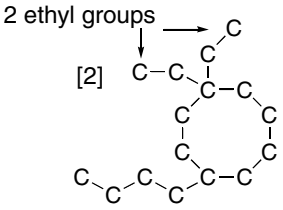


f. 4-butyl-1,1-diethyl**cyclooctane**

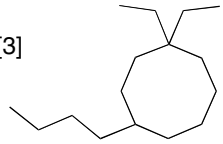
[1] 8 C cycloalkane



[2]

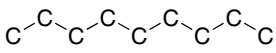


[3]

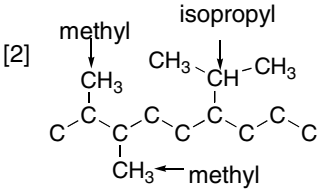


g. 6-isopropyl-2,3-dimethyl**nonane**

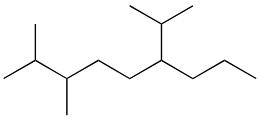
[1] 9 C alkane



[2]



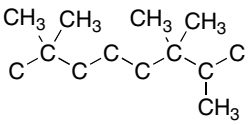
[3]



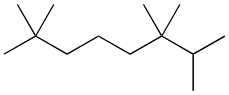
h. 2,2,6,6,7-pentamethyl**octane**

[1] 8 C alkane

[2] 5 methyl groups

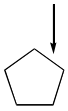


[3]

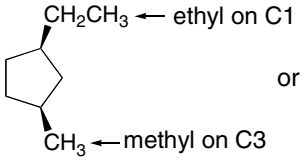


i. *cis*-1-ethyl-3-methyl**cyclopentane**

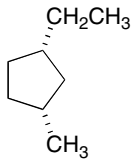
[1] 5 C ring



[2]

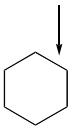


or

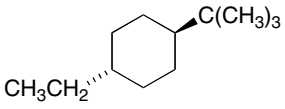


j. *trans*-1-*tert*-butyl-4-ethyl**cyclohexane**

[1] 6 C ring

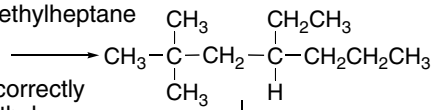


[2]



4.43 Draw the compounds.

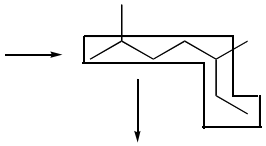
a. 2,2-dimethyl-4-ethylheptane



alphabetized incorrectly
ethyl before **m**ethyl

4-ethyl-2,2-dimethylheptane

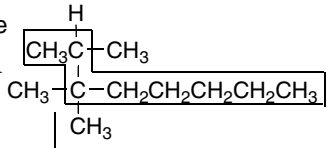
b. 5-ethyl-2-methylhexane



Longest chain was not chosen = **heptane**

2,5-dimethylheptane

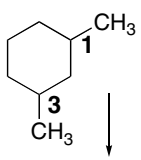
c. 2-methyl-2-isopropylheptane



Longest chain was not chosen = **octane**

2,3,3-trimethyloctane

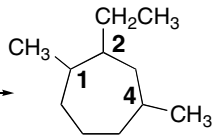
d. 1,5-dimethylcyclohexane



Numbered incorrectly.
Re-number so methyls are at C1 and C3.

1,3-dimethylcyclohexane

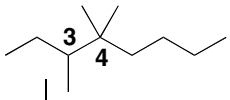
e. 1-ethyl-2,6-dimethylcycloheptane



Numbered incorrectly.
Re-number so methyls are at C1 and C4.

2-ethyl-1,4-dimethylcycloheptane

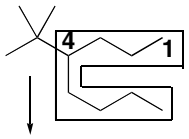
f. 5,5,6-trimethyloctane



Numbered incorrectly.
Re-number so methyls are at C3 and C4.

3,4,4-trimethyloctane

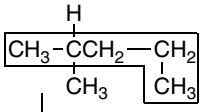
g. 3-butyl-2,2-dimethylhexane



Longest chain not chosen = **octane**

4-*tert*-butyloctane

h. 1,3-dimethylbutane

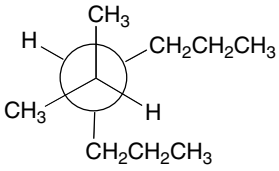


Longest chain not chosen = **pentane**

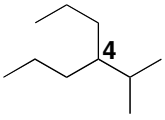
2-methylpentane

4.44

a.

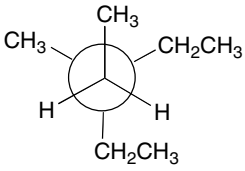


re-draw

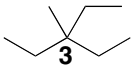


4-isopropylheptane

b.

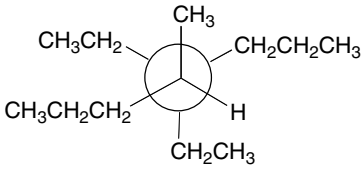


re-draw

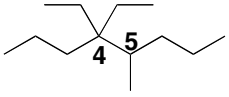


3-ethyl-3-methylpentane

c.



re-draw



4,4-diethyl-5-methyloctane

4.45 Use the rules from Answer 4.17.

a. $CH_3CH_2CH_3$ $CH_3CH_2CH_2CH_3$ $CH_3CH_2CH_2CH_2CH_3$

3C's 4 C's 5 C's

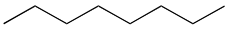
lowest boiling point **highest boiling point**

b. $(CH_3)_2CHCH(CH_3)_2$ $CH_3CH_2CH_2CH(CH_3)_2$ $CH_3(CH_2)_4CH_3$

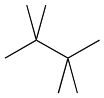
most branching least branching

lowest boiling point **highest boiling point**

4.46 a.



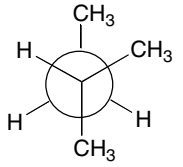
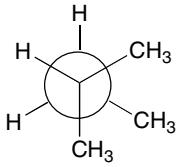
$CH_3(CH_2)_6CH_3$
no branching = higher surface area
higher boiling point



$(CH_3)_3CC(CH_3)_3$
branching = lower surface area
lower boiling point
more spherical, better packing =
higher melting point

b. There is a 159° difference in the melting points, but only a 20° difference in the boiling points because the symmetry in $(CH_3)_3CC(CH_3)_3$ allows it to pack more tightly in the solid, thus requiring more energy to melt. In contrast, once the compounds are in the liquid state, symmetry is no longer a factor, the compounds are isomeric alkanes, and the boiling points are closer together.

4.47

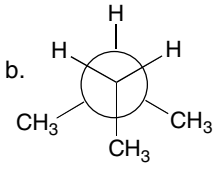
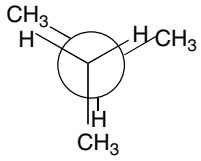
a.  or 

1 gauche CH_3,CH_3
= 3.8 kJ/mol
of destabilization

higher energy
2 gauche CH_3,CH_3
3.8 kJ/mol x 2 = 7.6 kJ/mol
of destabilization

Energy difference =

7.6 kJ/mol – 3.8 kJ/mol = **3.8 kJ/mol**

b.  or 

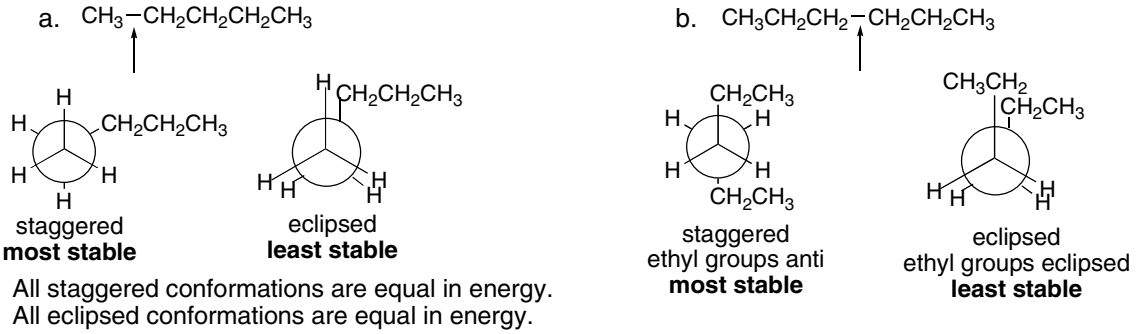
2 gauche CH_3,CH_3
3.8 kJ/mol x 2 =
7.6 kJ/mol
of destabilization

higher energy
3 eclipsed H,CH_3
6 kJ/mol x 3 = 18 kJ/mol
of destabilization

Energy difference =

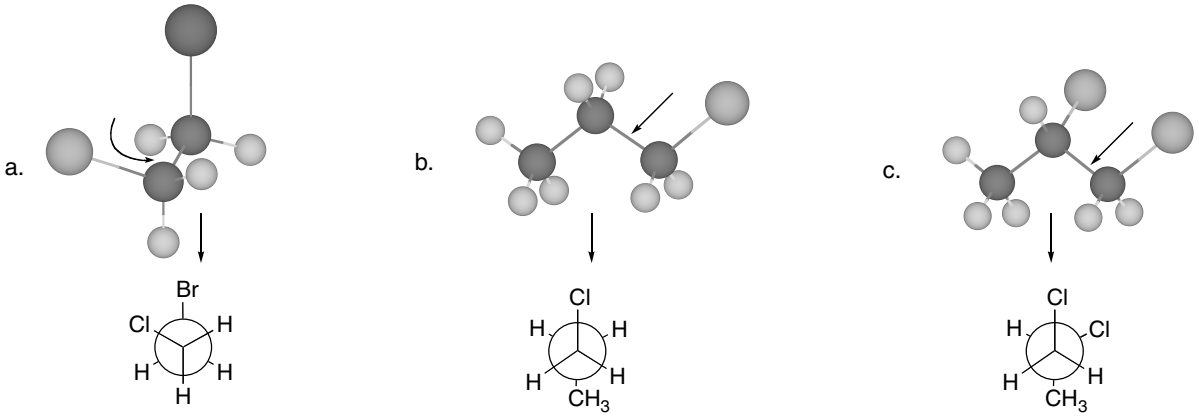
18 kJ/mol – 7.6 kJ/mol = **10.4 kJ/mol**

4.48 Use the rules from Answer 4.21 to determine the most and least stable conformations.

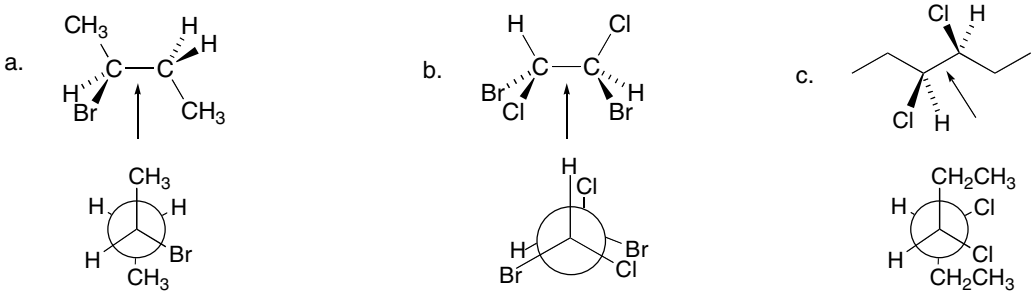


All staggered conformations are equal in energy.
All eclipsed conformations are equal in energy.

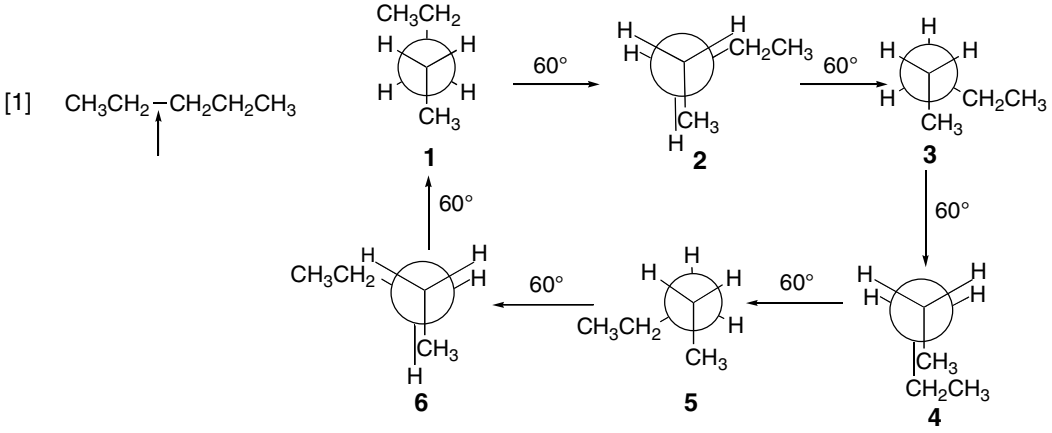
4.49

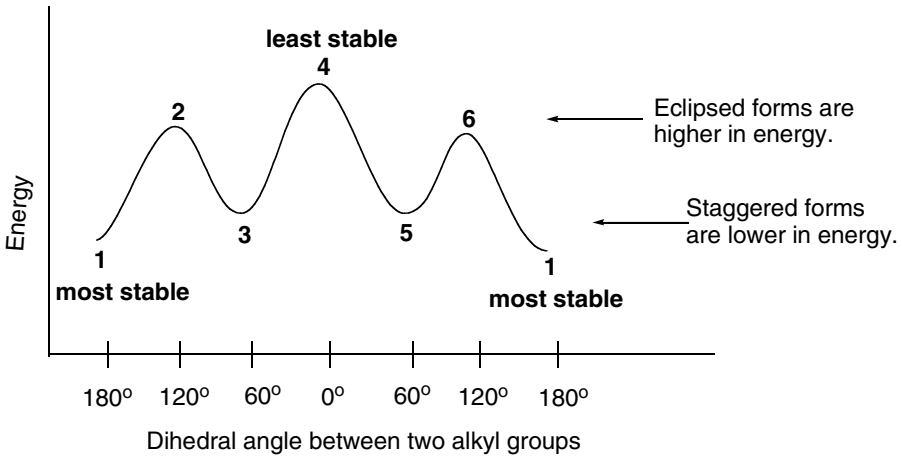


4.50

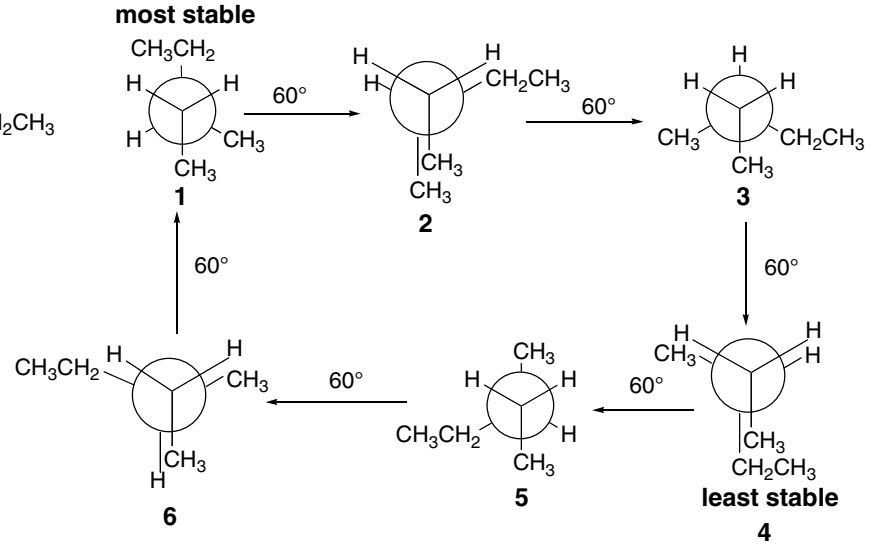


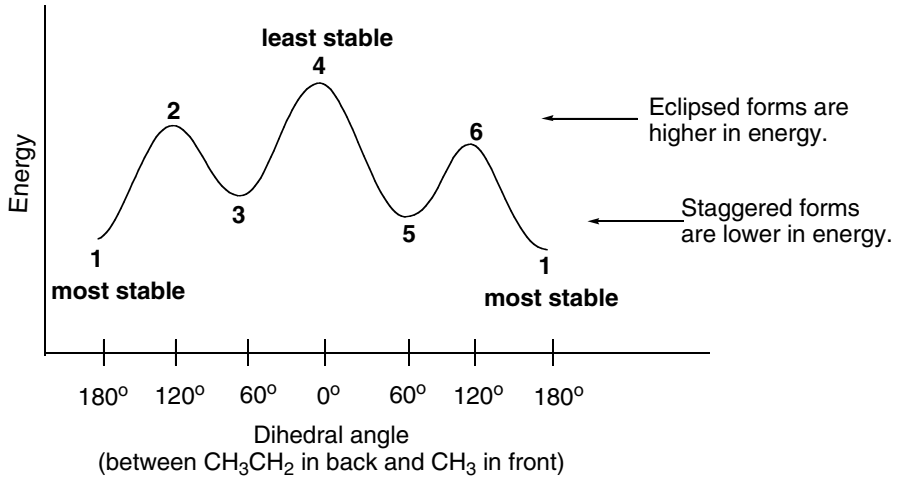
4.51





[2] $CH_3CH_2-\underset{\uparrow}{C}HCH_2CH_3$ ($\uparrow$ = CH_3)

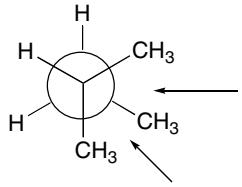




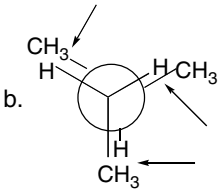
4.52 Two types of strain:

4.1 *Torsional strain* is due to eclipsed groups on adjacent carbon atoms.

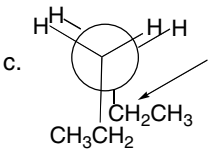
4.2 *Steric strain* is due to overlapping electron clouds of large groups (ex: gauche interactions).

a. 

two sites
three bulky methyl groups close =
steric strain

b. 

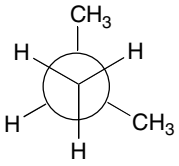
eclipsed conformation =
torsional strain

c. 

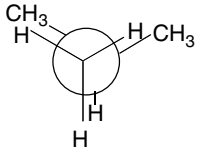
two bulky ethyl groups close =
steric strain
eclipsed conformation =
torsional strain

4.53 The barrier to rotation is equal to the difference in energy between the highest energy eclipsed and lowest energy staggered conformations of the molecule.

a. $CH_3-CH(CH_3)_2$



most stable



least stable

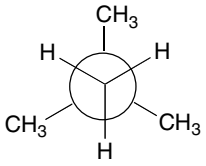
Destabilization energy =

2 H,CH_3 eclipsing interactions
2(6.0 kJ/mol) = 12.0 kJ/mol
1 H,H eclipsing interaction = 4.0 kJ/mol

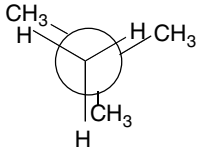
Total destabilization = **16.0 kJ/mol**

16.0 kJ/mol = rotation barrier

b. $CH_3-C(CH_3)_3$



most stable



least stable

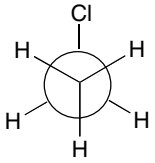
Destabilization energy =

3 H,CH_3 eclipsing interactions
3(6.0 kJ/mol) = 18.0 kJ/mol

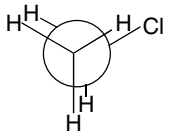
Total destabilization = **18.0 kJ/mol**

18.0 kJ/mol = rotation barrier

4.54



most stable



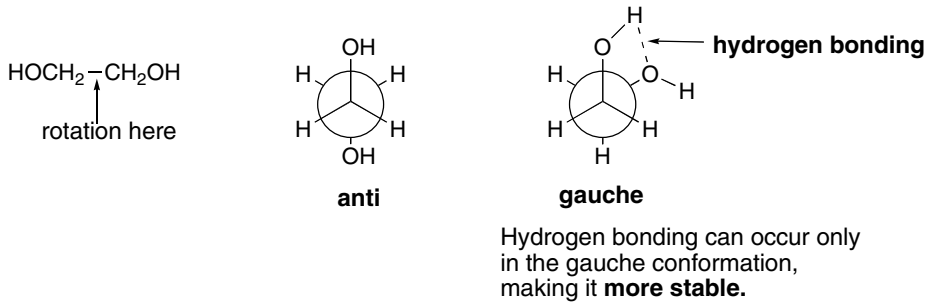
least stable

2 H,H eclipsing interactions = 2(4.0 kJ/mol) = 8.0 kJ/mol

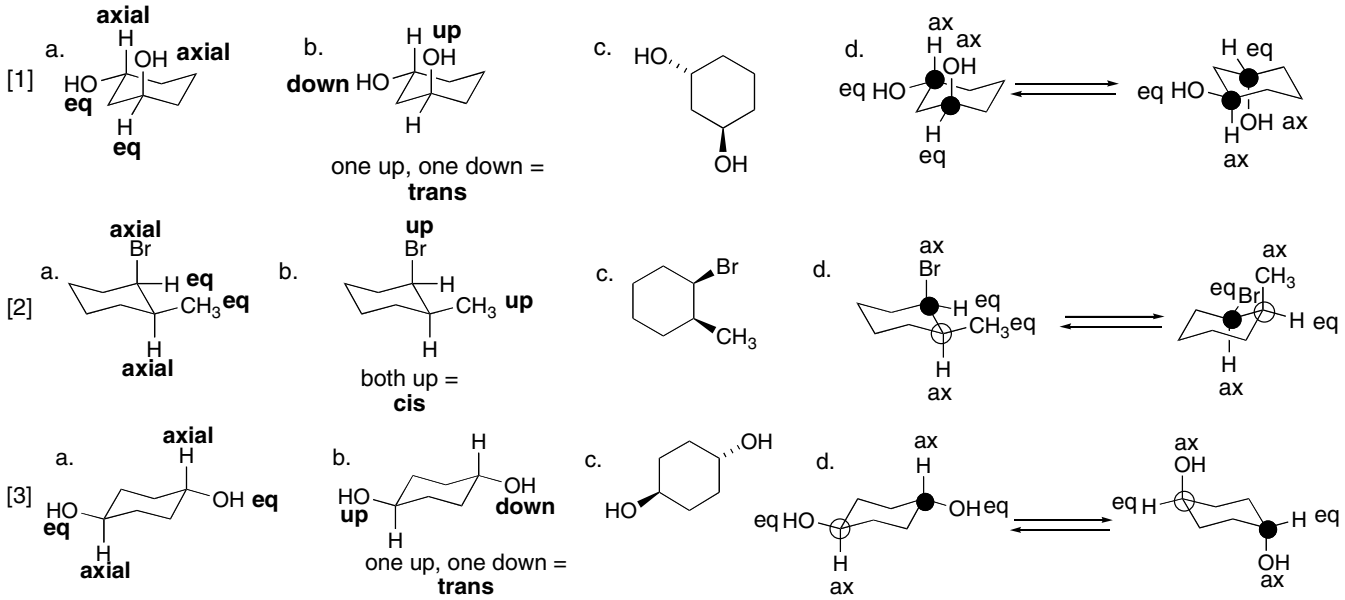
Since the barrier to rotation is 15 kJ/mol, the difference between this value and the destabilization due to H,H eclipsing is the destabilization due to H,Cl eclipsing.

15.0 kJ/mol – 8.0 kJ/mol = 7.0 kJ/mol
destabilization due to H,Cl eclipsing

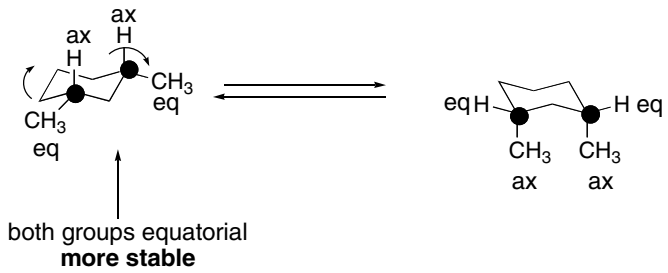
4.55 The gauche conformation can intramolecularly hydrogen bond, making it the more stable conformation.



4.56



4.57

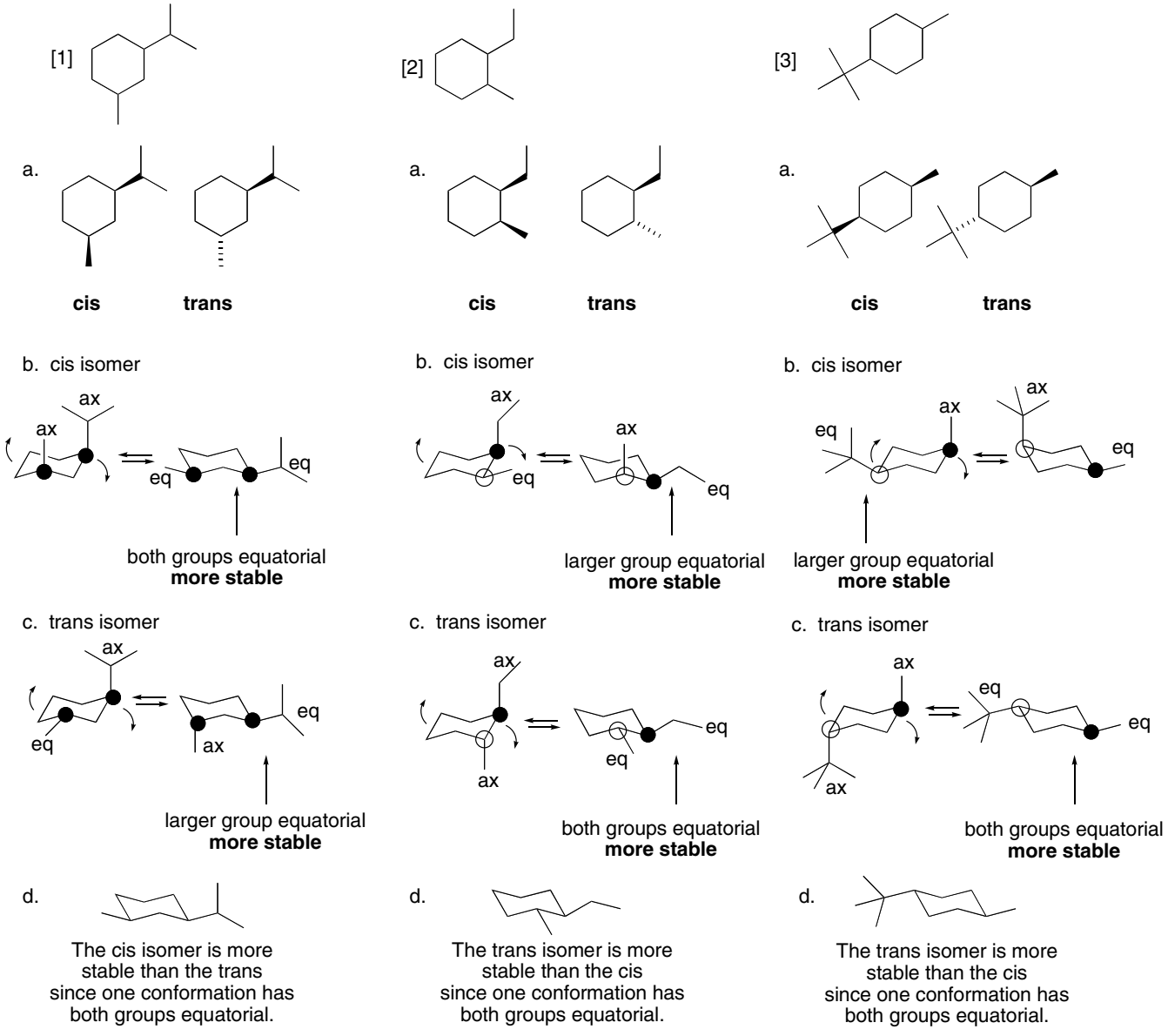


4.58

Axial/equatorial substituent location

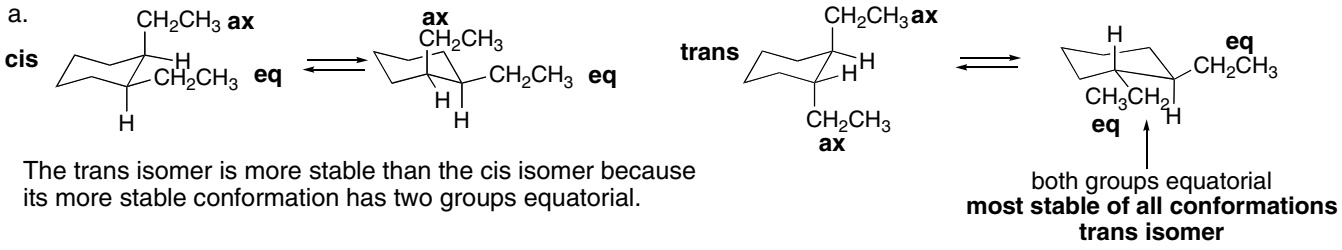
Disubstituted cyclohexane	Conformation 1	Conformation 2
a. 1,2-cis disubstituted	Axial/equatorial	Equatorial/axial
b. 1,2-trans disubstituted	Axial/axial	Equatorial/equatorial
c. 1,3-cis disubstituted	Axial/axial	Equatorial/equatorial
d. 1,3-trans disubstituted	Axial/equatorial	Equatorial/axial
e. 1,4-cis disubstituted	Axial/equatorial	Equatorial/axial
f. 1,4-trans disubstituted	Axial/axial	Equatorial/equatorial

4.59 A **cis isomer** has two groups on the **same side** of the ring. The two groups can be drawn both up or both down. Only one possibility is drawn. A **trans isomer** has one group on one side of the ring and one group on the other side. Either group can be drawn on either side. Only one possibility is drawn.



4.60 Compare the isomers by drawing them in chair conformations. Equatorial substituents are more stable. See the definitions in Problem 4.59.

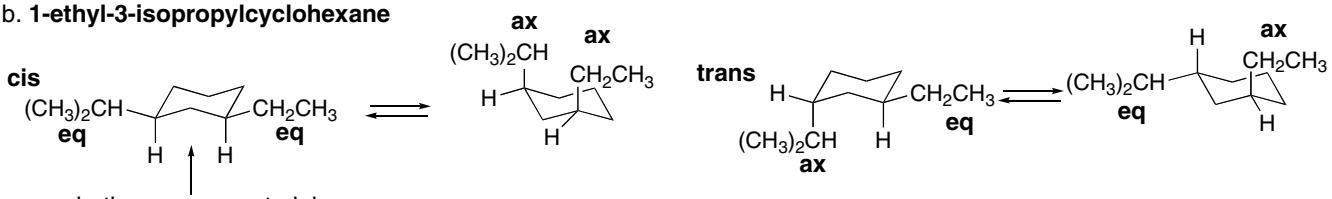
a.



The trans isomer is more stable than the cis isomer because its more stable conformation has two groups equatorial.

both groups equatorial
most stable of all conformations
trans isomer

b. **1-ethyl-3-isopropylcyclohexane**

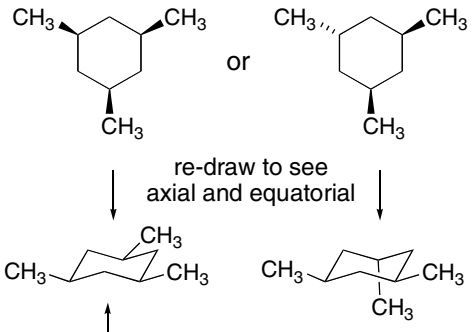


both groups equatorial
most stable of all conformations
cis isomer

The cis isomer is more stable than the trans isomer because its more stable conformation has two groups equatorial.

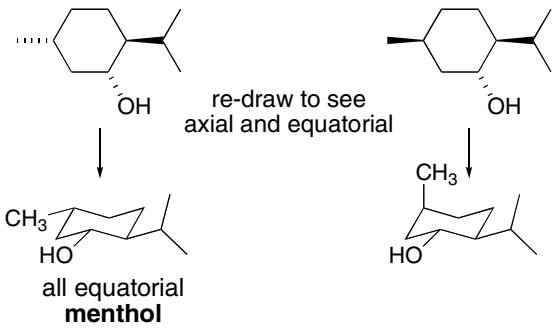
4.61

Only the more stable conformation is drawn.



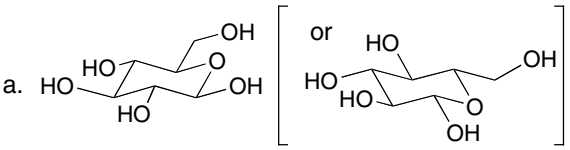
more stable
substituents on C1, C3, C5 =
all equatorial

4.62

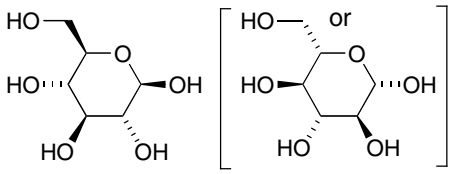


all equatorial
menthol

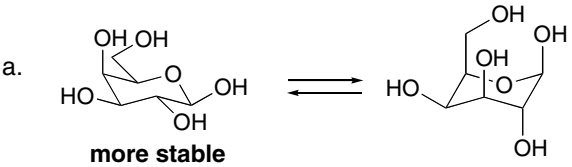
4.63

a. 

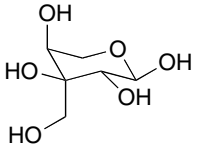
most stable
All groups are equatorial.

b. 

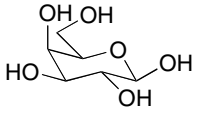
4.64

a. 

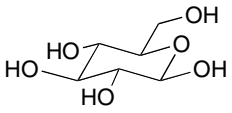
more stable
More groups are equatorial.

c. 

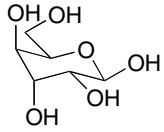
constitutional isomer

b. 

galactose

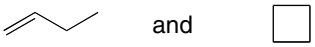


glucose
All groups are equatorial.
more stable

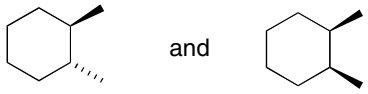
d. 

stereoisomer

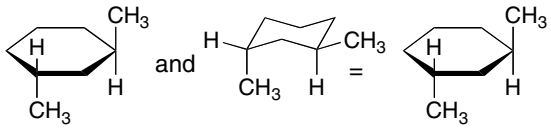
4.65

a. 

same molecular formula C_4H_8
different connectivity
constitutional isomers

b. 

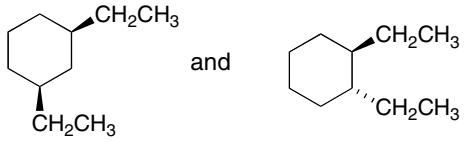
different arrangement in three dimensions
stereoisomers

c. 

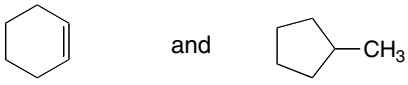
1 down, 1 up = **trans**

1 down, 1 up = **trans**

same arrangement in three dimensions
identical

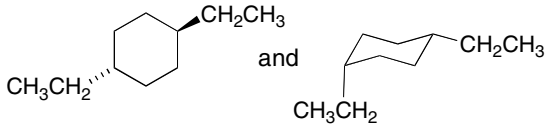
d. 

same molecular formula $C_{10}H_{20}$
different connectivity
constitutional isomers

e. 

molecular formula: C_6H_{10} **molecular formula: C_6H_{12}**

different molecular formulas
not isomers

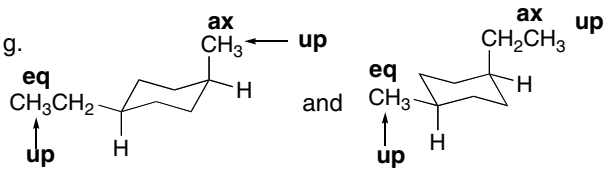
f. 

1 down, 1 up = **trans**

both down = **cis**

different arrangement in three dimensions
stereoisomers

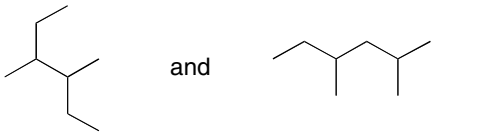
g.



both up = **cis** both up = **cis**

same arrangement in three dimensions
identical

h.

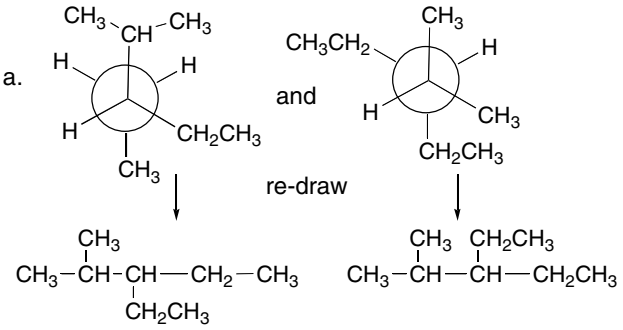


3,4-dimethylhexane and **2,4-dimethylhexane**

same molecular formula C_8H_{18}
different IUPAC names
constitutional isomers

4.66

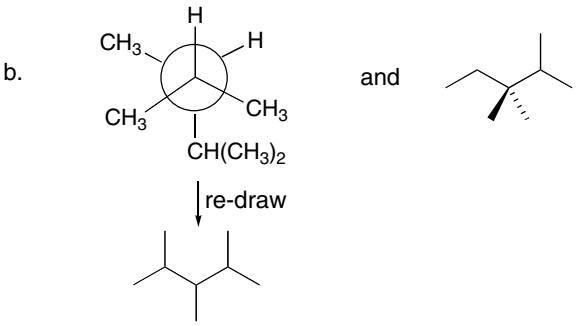
a.



3-ethyl-2-methylpentane 3-ethyl-2-methylpentane

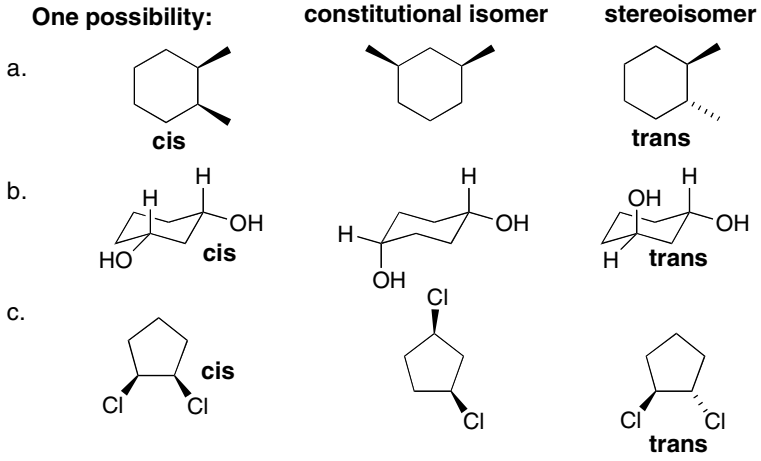
same molecular formula
same name
identical molecules

b.



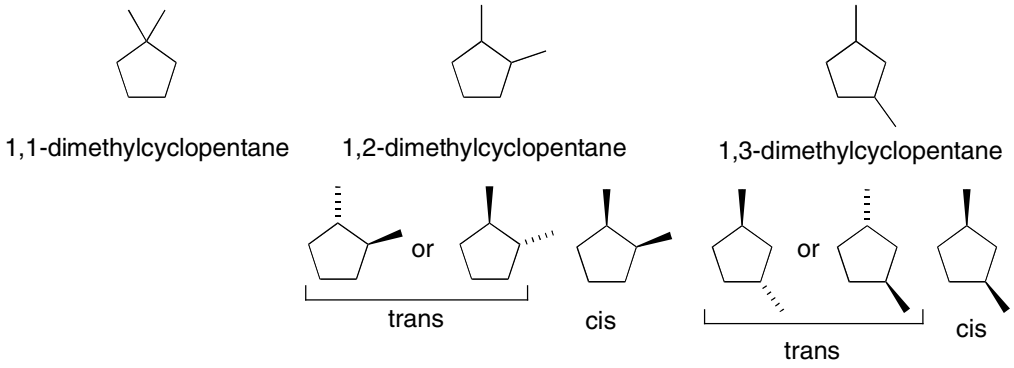
same molecular formula
different arrangement of atoms
constitutional isomers

4.67



4.68

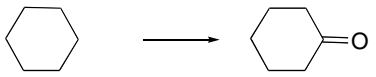
Three constitutional isomers of C_7H_{14}:



4.69 Use the definitions from Answer 4.32 to classify the reactions.

a. $CH_3CHO \xrightarrow{} CH_3CH_2OH$

Decrease in the number of C–O bonds. **Reduction**

b. 

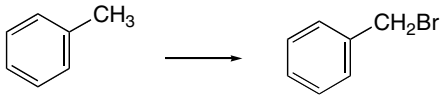
Increase in the number of C–O bonds. **Oxidation**

c. $CH_2{=}CH_2 \xrightarrow{} HOCH_2CH_2OH$

Two new C–O bonds. **Oxidation**

d. $CH_2{=}CH_2 \xrightarrow{} H{-}C{\equiv}C{-}H$

Decrease in the number of C–H bonds. **Oxidation**

e. 

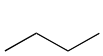
Increase in the number of C–Z bonds. **Oxidation**

f. $CH_3CH_2OH \xrightarrow{} CH_2{=}CH_2$

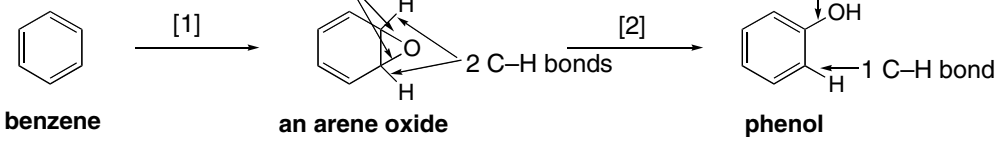
Loss of one C–O bond *and* one C–H bond. **Neither**

4.70 Use the rule from Answer 4.33.

a. $CH_3CH_2CH_2CH_2CH(CH_3)_2 \xrightarrow[11\ O_2]{\text{flame}} 7\ CO_2 + 8\ H_2O + \text{heat}$

b.  $\xrightarrow[(13/2)\ O_2]{\text{flame}} 4\ CO_2 + 5\ H_2O + \text{heat}$

4.71

a. 

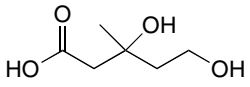
benzene — **an arene oxide** — **phenol**

[1] increase in C–O bonds
oxidation reaction

[2] loss of 1 C–O bond,
loss of 1 C–H bond
neither

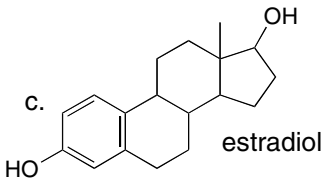
b. Phenol is more water soluble than benzene because it is **polar (contains an O–H group) and can hydrogen bond with water,** whereas benzene is nonpolar and cannot hydrogen bond.

4.72 Lipids contain many nonpolar C–C and C–H bonds and few polar functional groups.

a. 

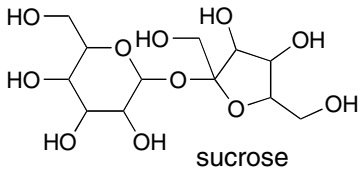
mevalonic acid

many polar functional groups
not a lipid

c. 

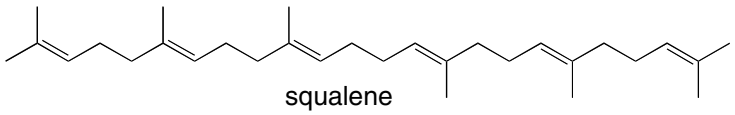
estradiol

few polar functional groups
a lipid

d. 

sucrose

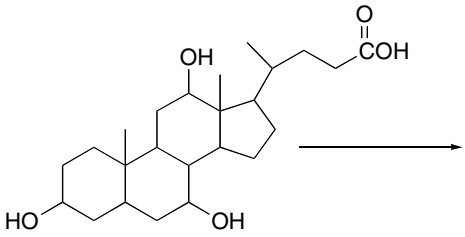
many polar functional groups
not a lipid

b. 

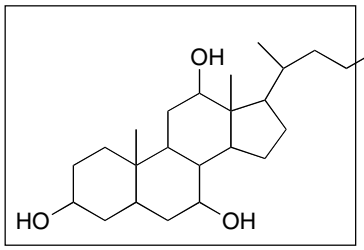
squalene

no polar functional groups
a lipid

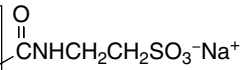
4.73



cholic acid
a bile acid



a bile salt

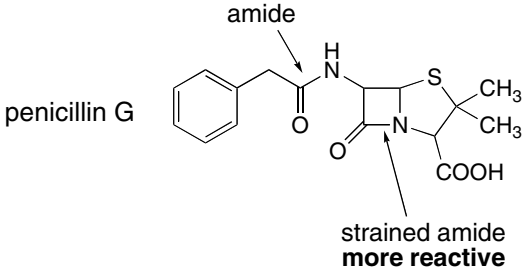


This polar part of the molecule
interacts with water.

This nonpolar part of the molecule
can **interact with lipids** to create
micelles that allow for transport
of lipids through aqueous environments.

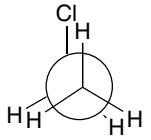
4.74 The mineral oil can prevent the body's absorption of important fat-soluble vitamins. The vitamins dissolve in the mineral oil, and are thus not absorbed. Instead, they are expelled with the mineral oil.

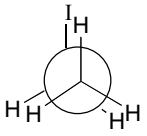
4.75 The amide in the four-membered ring has 90° bond angles giving it angle strain, and therefore making it more reactive.



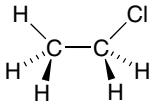
4.76

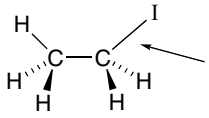
Example:



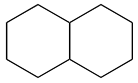


Although I is a much bigger atom than Cl, the C–I bond is also much longer than the C–Cl bond. As a result the eclipsing interaction of the H and I atoms is not very much different in magnitude from the H,Cl eclipsing interaction.

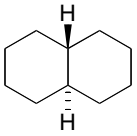




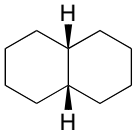
4.77



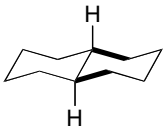
decalin



trans-decalin

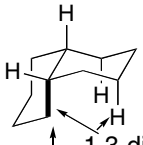


cis-decalin



trans

The trans isomer is more stable since the carbon groups at the ring junction are both in the favorable equatorial position.

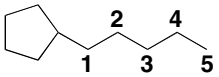


1,3-diaxial interaction

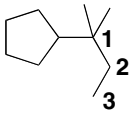
cis

This bond is axial, creating unfavorable 1,3-diaxial interactions.

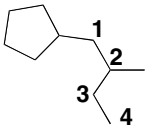
4.78



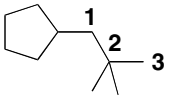
pentylcyclopentane



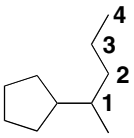
(1,1-dimethylpropyl)cyclopentane



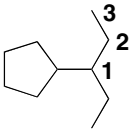
(2-methylbutyl)cyclopentane



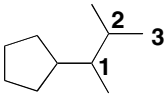
(2,2-dimethylpropyl)cyclopentane



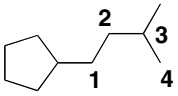
(1-methylbutyl)cyclopentane



(1-ethylpropyl)cyclopentane



(1,2-dimethylpropyl)cyclopentane



(3-methylbutyl)cyclopentane