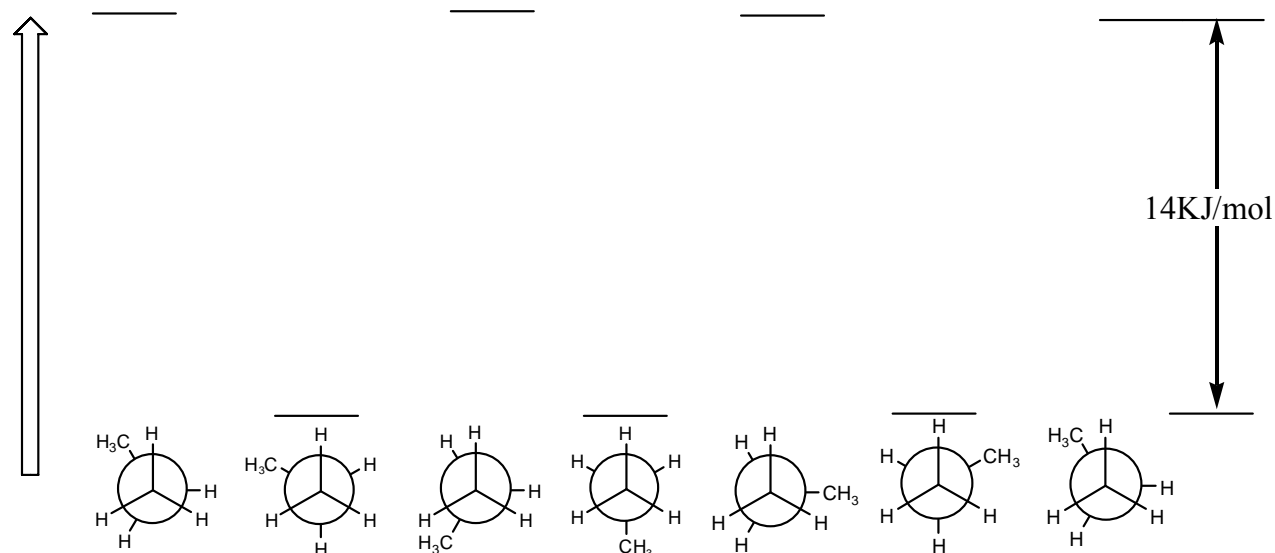


Chapter 4

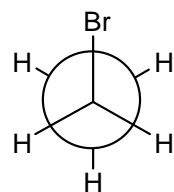
4.1 Make a graph of potential energy versus angle of bond rotation for propane, and assign values to the energy maxima.

Solution:

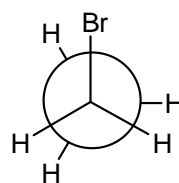


4.2 Draw Newman projections of the most stable and least stable conformations of bromoethane.

Solution:



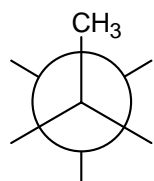
Most stable



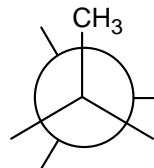
least stable

4.3 Consider 2-methylpropane (isobutane). Sighting along the C2-C1 bond.

(a) Draw a Newman projection of the most stable conformation.



(b) Draw a Newman projection of the least stable conformation

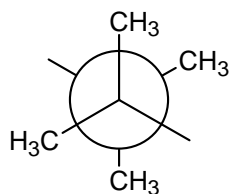


(c) Make a graph of the energy versus angles of rotations around the C2-C1 bond:

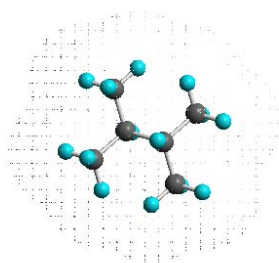
(d) Since a hydrogen-hydrogen eclipsing interaction costs 4.0 kJ/mol and a hydrogen-methyl eclipsing interaction cost 6.0 kJ/mol, assign reactive values to the maxima and minima in your graph.

4.4 Sight along the C2-C3 bond of 2,3-dimethylbutane, and draw a Newman projection of the most stable conformation.

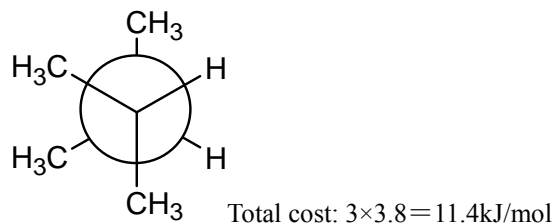
Solutions:



4.5 Draw a Newman projection along the C2-C3 bond of the following conformation of 2,3-dimethylbutane, and calculate a total strain energy:



Solution:



4.6 Figure 4.8 shows that cyclopropane is more strained than cyclohexane by 115 kJ/mol. Which has the higher heat of combustion on a per-gram basis, cyclopropane or cyclohexane?

Solution:

Because the more strained energy the compound contains, the more energy is released on combustion, cyclopropane has the higher heat of a combustion on a per-gram basis.

4.7 Each hydrogen-hydrogen eclipsing interaction in ethane costs about 4.0 kJ/mol. How many such interactions are present in cyclopropane? What fraction of the overall 115 kJ/mol (27.5 kcal/mol) strain energy of cyclopropane is due to torsional strain?

Solution:

Six.

$$4.0 \times 6 / 115 = 20.9\%$$

4.8 cis-1,2-Dimethylcyclopropane has a larger heat of combustion than trans-1,2-dimethylcyclopropane. How can you account for this difference? Which of the two compounds is more stable?

Solution:

Because the methyl group eclipses each other in the cis isomer.

The trans isomer is more stable.

4.9 How many hydrogen-hydrogen eclipsing interactions would be present if cyclopentane were planar?

Assuming an energy cost of 4.0 KJ/mol for each eclipsing interactions, how much torsional strain would planar cyclopentane have? How much of this strain is relieved by puckering if the measured total strain of cyclopentane is 26.0 KJ/mol?

Solution:

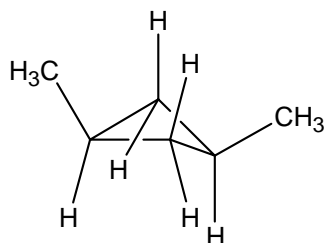
(1) 10

(2) $W=4 \times 10=40$ KJ/mol

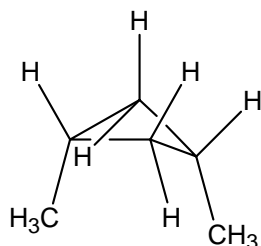
(3) $c\%=(40-26)/40 \times 100\%=35\%$

4.10 Two conformations of cis-1,3-dimethylcyclobutane are shown. What is the difference between them, and which do you think is likely to be more stable?

(a)



(b)



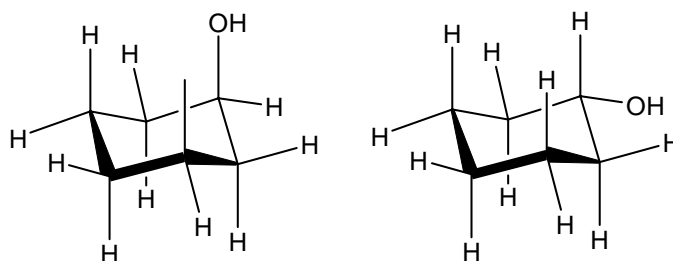
Solution:

They are conformation isomers.

(a) is more stable., Because the methyl groups are farther apart.

4.11 Draw two different chair conformations of cyclohexanol, showing all hydrogen atoms. Identify each position as axial or equatorial.

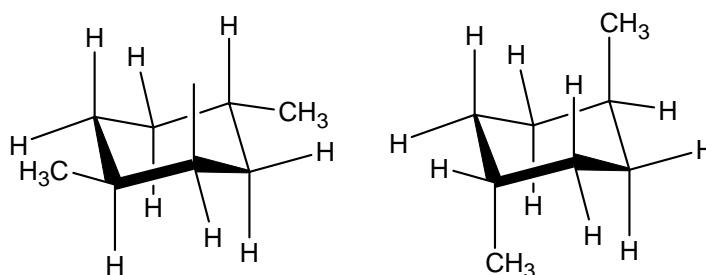
Solution:



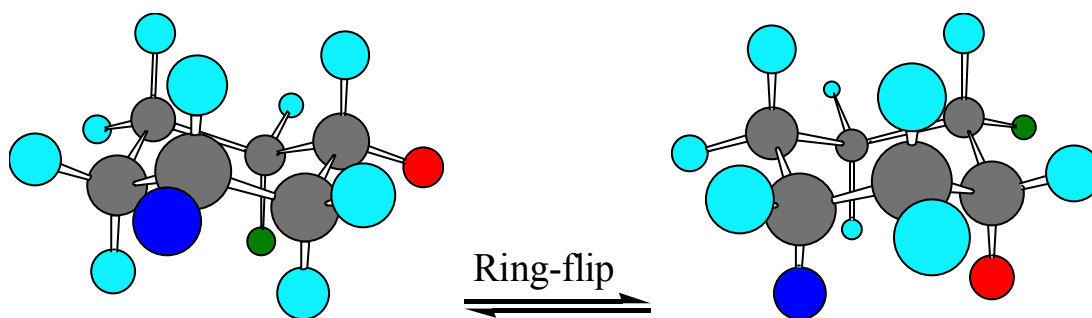
4.12 Draw two different chair conformations of trans-1,4-dimethylcyclohexane, and label all positions

as axial or equatorial.

Solution:

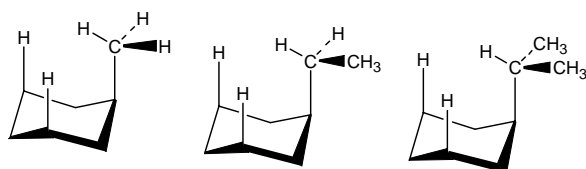


4.13 Identify each of the colored positions—red, blue, and green—as axial or equatorial. Then carry out a ring—flip, and show the new positions occupied by each color.

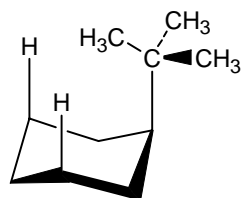


4.14 How can you account for the fact (Table 4.2) that an axial tert-butyl substituent has much larger 1,3-diaxial interactions than isopropyl, but isopropyl is fairly similar to ethyl and methyl? Use molecular models to help with your answer.

Solution:

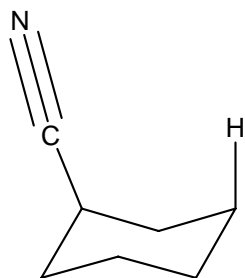


With a methyl, ethyl and propyl group, a hydrogen points in toward the ring. But with a butyl group, a methyl group points in.



4.15 Why do you suppose an axial cyano substituent causes practically no 1,3-diaxial steric strain (0.4kJ/mol)? Use molecular model to help with your answer.

Solution:



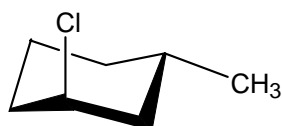
Because of the nitrogen-carbon triple bond the electron density between N and C atoms is high, the distance between cyano substituent and hydrogen gets larger. The interaction between them becomes weaker.

4.16 Look at Figure 4.18 and estimate the percentages of axial and equatorial conformers present at equilibrium in bromocyclohexane.

Solution: the percentage of axial conformer is about 27%, while the percentage of equatorial conformer is about 73% at equilibrium.

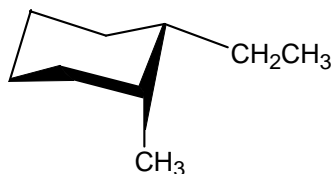
4.17 Draw the most stable chair conformation of the following molecules, and estimate the amount of strain in each:

(a) trans-1-Chloro-3-methylcyclohexane



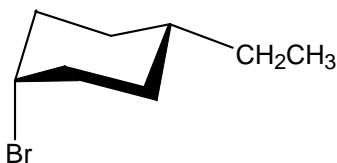
$$\text{strain} = 2 \times 1.0 = 2.0 \text{ kJ/mol}$$

(b) cis-1-Ethyl-2-methylcyclohexane



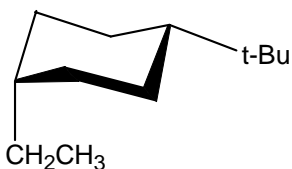
$$\text{Strain} = 2 \times 3.8 + 3.8 = 11.4 \text{ kJ/mol}$$

(c) cis-1-Bromo-4-ethylcyclohexane



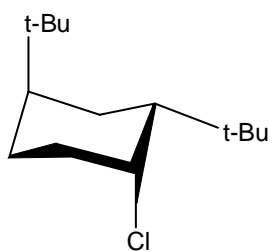
$$\text{Strain} = 2 \times 1.0 = 2.0 \text{ kJ/mol}$$

(d) cis-1-tert-Butylcyclohexane



$$\text{Strain} = 2 \times 4.0 = 8.0 \text{ kJ/mol}$$

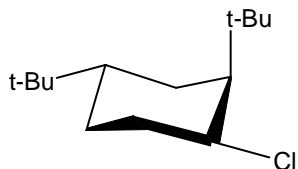
4.18 Name the following compound, identify each substituent as axial or equatorial, and tell whether the conformation shown is the more stable or less stable chair form:



Solution: The compound is 2,4-Di-tert-butyl-1-chloro-cyclohexane.

The tert-butyl on the left and Cl are axial, the tert-butyl on the right is equatorial.

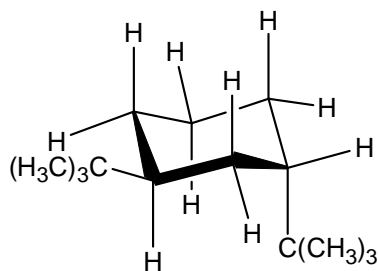
The conformation shown is the less stable chair form, the more stable one is as follows:



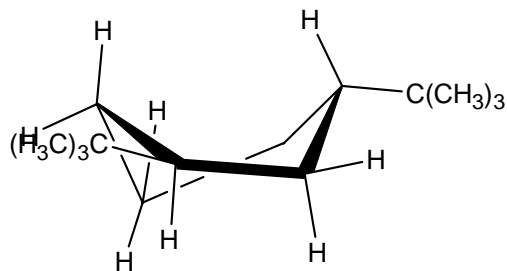
4.19 trans-1,3-Di-tert-butylcyclohexane is one of the few molecules that exists largely in a twist-boat conformation. Draw both a chair conformation and the likely twist-boat conformation, and then explain why the twist-boat form is favored.

Solution:

Chair conformation



Twist-boat conformation



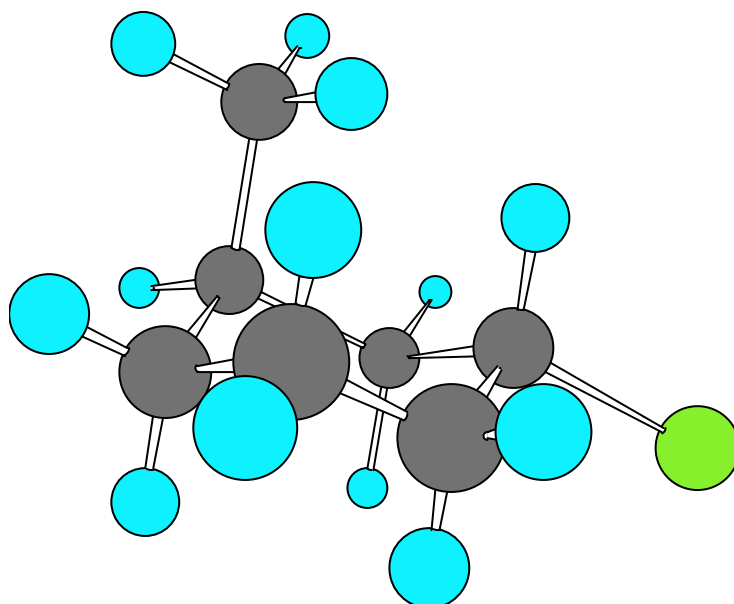
In the chair conformation One of the substituents is in the axial position and the steric strain is large. In the twist-boat conformation the two substituents are both in the equatorial positions and the some strain is relieved.

4.20 Which isomer is more stable, cis-decalin or trans-decalin? Explain.

Solution:

Cis-decalin is less stable, because of the steric strain.

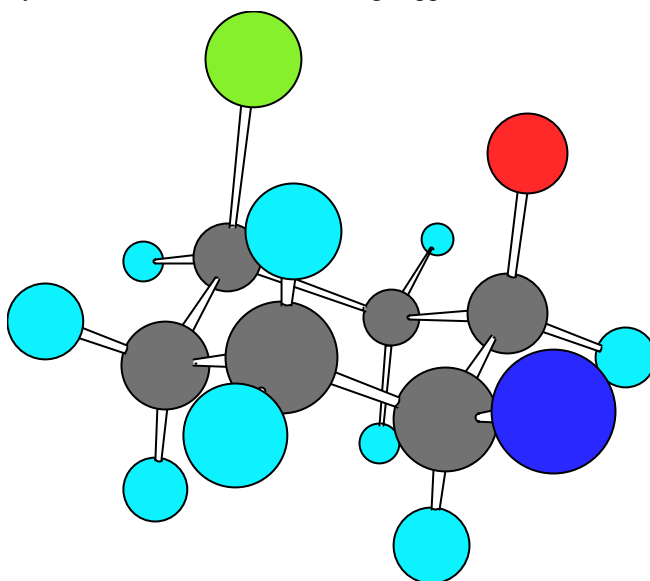
4.21 Name the following compound, identify each substituent as axial or equatorial, and tell whether the conformation shown is the more stable or less stable chair form.



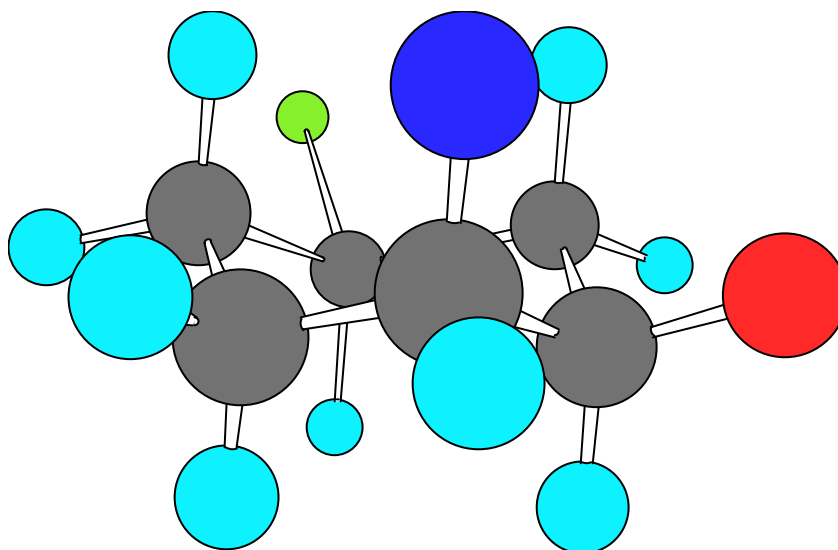
SOLUTION: the name: 1-chloro-3-methylcyclohexane

It is less stable chair form.

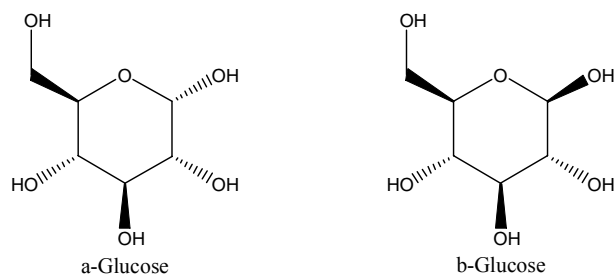
4.22 A trisubstituted cyclohexane with three substituents---red, yellow, and blue---undergoes a ring-flip to its alternative chair conformation. Identify each substituent as axial or equatorial, and show the positions occupied by the three substituents in the ring-flipped form.



SOLUTION: The ring-flip production:



4.23 Glucose exists in two forms having a 36:64 ratio at equilibrium. Draw a skeletal structure if each, describe the difference between them and tell which of the two you think is more stable.



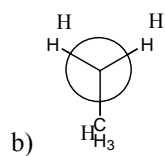
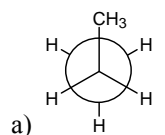
Solution:

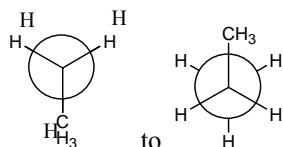
B-Glucose is more stable, for a-Glucose have more torsional strain between the two C-O bonds on the same side.

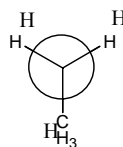
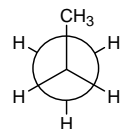
4.24 Consider 2-methylbutane (isopentane). Sighting along the C2-C3 bond:

- Draw a Newman projection of the most stable conformation.
- Draw a Newman projection of the least stable conformation.
- Since a CH₃-CH₃ eclipsing interaction costs 11KJ/mol and a CH₃-CH₃ gauche interaction cost 3.8KJ/mol, make a quantitative plot of energy versus rotation about the C2-C3 bond.

Solution:





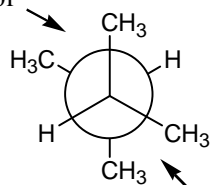
c) Rotate from  to , the energy will be $11\text{kJ/mol} - 3.8\text{kJ/mol} = 7.2\text{kJ/mol}$

4.25 What are the relative energies of the three possible staggered conformations around the C2-C3 bond in 2,3-dimethylbutane? (See Problem 4.24)

Solution:

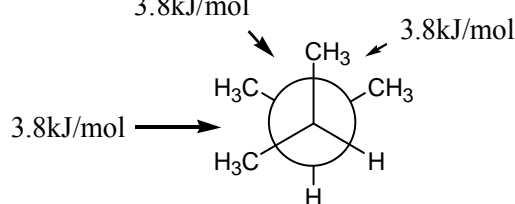
3.8kJ/mol ($3.8 \times 3 - 3.8 \times 2$)

3.8kJ/mol



3.8kJ/mol

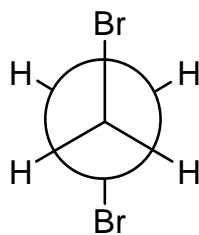
3.8kJ/mol



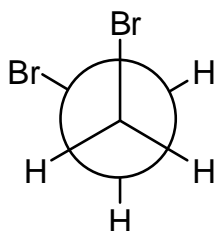
4.26 Construct a qualitative potential-energy diagram for rotation about the C-C bond of 1,2-dibromoethane. Which conformation would you expect to be more stable? Label the anti and gauche conformations of 1,2-dibromoethane.

Solution:

The curve is similar to *Figure 4.5* with different data.



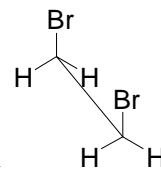
anti



gauche

The *anti* form is more stable.

4.27 Which conformation of 1,2-dibromoethane (Problem 4.26) would you expect to have the large dipole moment? The observed dipole moment is $\mu = 1.0\text{ D}$. What does this tell you about the actual structure of the molecule?



Solution: For 1,2-dibromoethane the completely eclipsed conformation

will have the larger dipole moment. But the observed dipole moment tells us that the actual structure of the molecule is changeable, the conformations convert constantly.

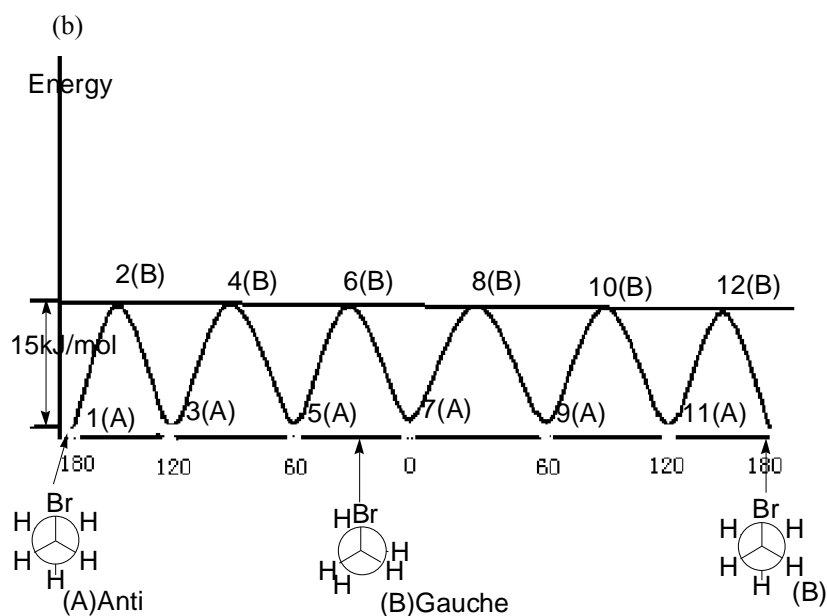
4.28 The barrier to rotation about the C-C bond in bromoethane is 15 kJ/mol (3.6 kcal/mol).

(a) What energy value can you assign to a H-Br eclipsing interaction?

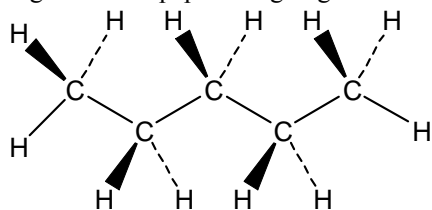
(b) Construct a quantitative diagram of potential energy versus amount of bond rotation for bromoethane.

Solution:

(a) We can assign a value of $15 - (2 \times 4) = 7.0\text{kJ/mol}$ to an H-Br eclipsing interaction.

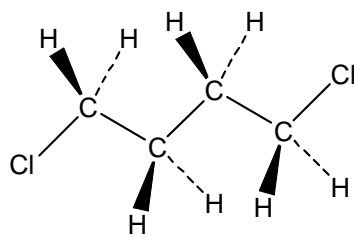


4.29: Draw the most stable conformation of pentane, using wedges and dashes to represent bonds coming out of the paper and going behind the paper, respectively.



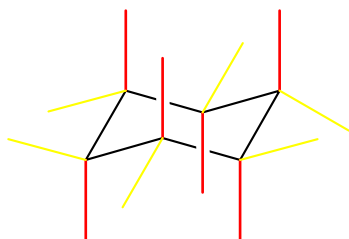
Solution:

4.30: Draw the most stable conformation of 1,4-dichlorobutane, using wedges and dashes to represent bonds coming out of the paper and going behind the paper, respectively.



Solution:

4.31 Draw a chair cyclohexane ring, and label all positions as axial or equatorial.



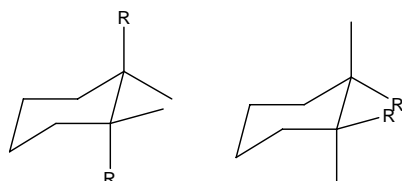
The red bonds represent axial positions, and the yellow ones represent equatorial positions.

4.32 A cis-1,2-disubstituted cyclohexane such as cis-1,2-dichloro-cyclohexane, must have one group axial and one group equatorial. Explain.

Solution: Because there are just two kinds of carbon hydrogen bonds, and there are just one equatorial bond and one axial bond on the same face of the two adjacent carbons.

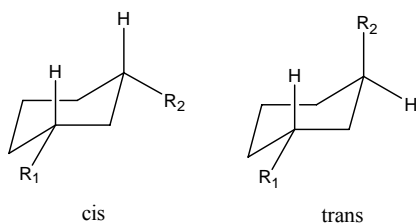
4.33 A trans-1, 2-disubstituted cyclohexane must either have both groups axial or both groups equatorial. Explain.

Solution: The structure of trans-1, 2-disubstituted cyclohexane will only be following, they could not be one is axial and the other is equatorial, that is cis isomers.

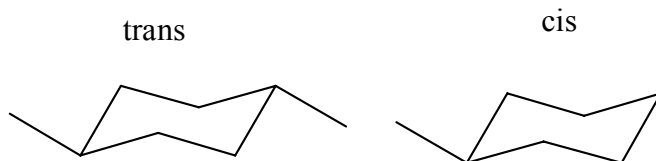


4.34 Why is a cis-1, 3-disubstituted cyclohexane more stable than its trans isomer?

Solution: In trans isomer, there will be torsional strain between R_2 and H, so the cis isomer is more stable.



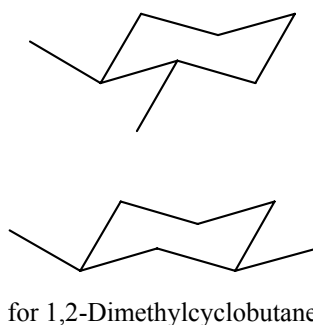
4.35 Which is more stable, a trans-1,4-disubstituted cyclohexane or its cis isomer?



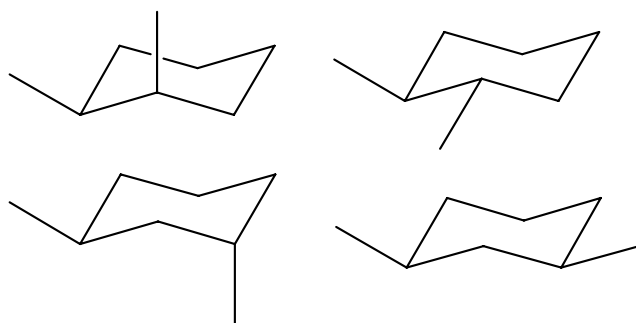
trans-1,4-disubstituted cyclohexane is more stable. For the cis one has steric strain of $3.8 \times 2 = 7.6 \text{ kJ/mol}$.

4.36 cis-1,2-Dimethylcyclobutane is less stable than its trans isomer, but cis-1,3-dimethylcyclobutane is more stable than its trans isomer. Draw the most stable conformations of both, and explain.

more stable



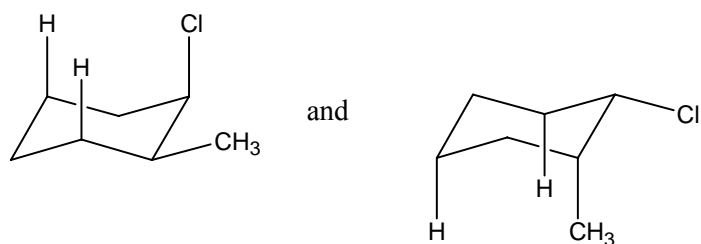
for 1,2-Dimethylcyclobutane



the front one has steric strain. So the second one is more stable.

4.37 Draw two chair conformations of cis-1-chloro-methylcyclohexane. Which is more stable, and by how much?

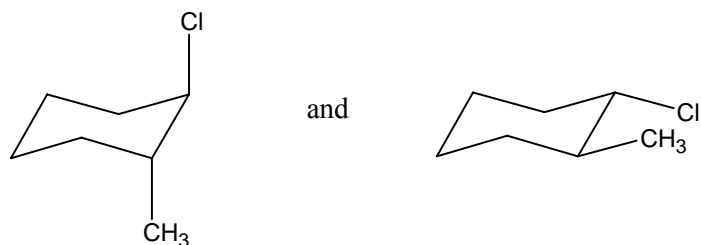
Solution:



The total strain for first one is $2 \times 1.0 = 2 \text{ kJ/mol}$, and the total strain for the second one is $2 \times 3.8 = 7.6 \text{ kJ/mol}$, so the second one is more stable than first one, by 5.6 kJ/mol .

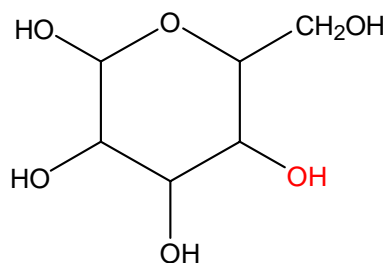
4.38 Draw two chair conformations of trans-1-chloro-methylcyclohexane. Which is more stable?

Solution:

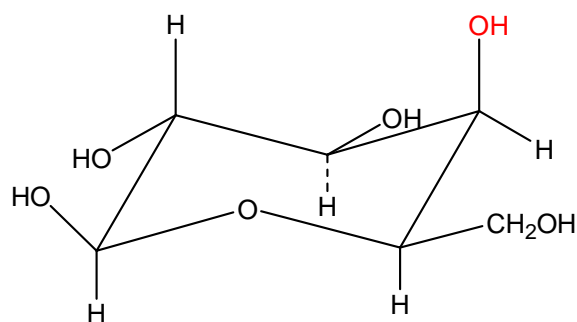


The second one is more stable.

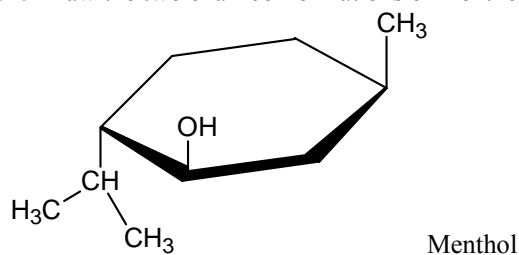
4.39 β -Galactose, a sugar related to glucose, contains a six-membered ring in which all the substituents except the $-\text{OH}$ group indicated below in red are equatorial. Draw β -galactose in its more stable chair conformation.



Galactose

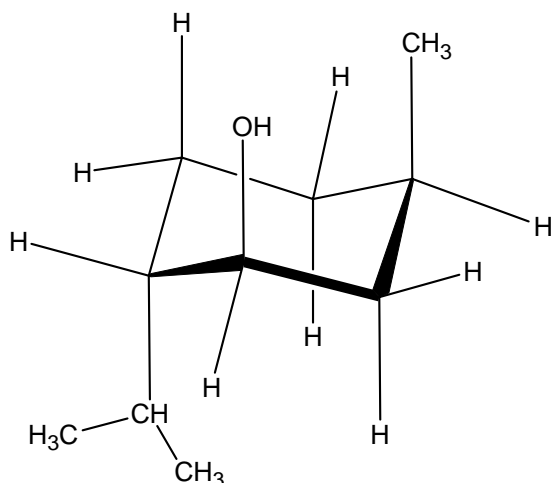


4.40 Draw the two chair conformations of menthol, and tell which is more stable.

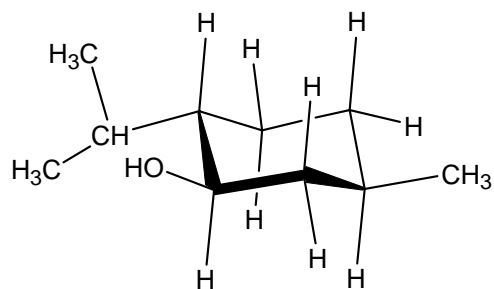


Solution:

The first one:



The second one:



The second one is more stable.

4.41 From the data in Figure 4.18 and Table 4.2, estimate the percentages of molecules that have their substituents in an axial orientation for the following compounds:

(a) Isopropylcyclohexane

(b) Fluorocyclohexane

(c) Cyclohexanecarbonitrile, $C_6H_{11}CN$

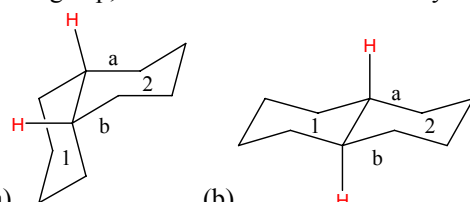
(d) Cyclohexanol, $C_6H_{11}OH$

Solution: (a) About 13%. (b) About 42%. (c) About 45%. (d) About 26%.

4.47: We saw in problem 4.20 that cis-decalin is less stable than trans-decalin. Assume that the 1,3-diaxial interactions in trans-decalin are similar to those in axial methylcyclohexane [that is, one CH₂-H interaction costs 3.8 kJ/mol(0.9kcal/mol)], and calculate the magnitude of the energy difference between cis- and trans-decalin.

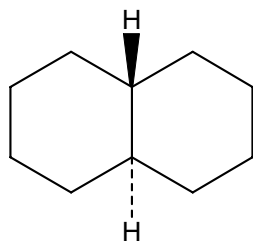
Solution: As there are four CH-H interactions, the total magnitude of the energy difference between cis- and trans-decalin is 15.2kJ/mol.

4.48: Using molecular model as well as structure drawings, explain why trans-decalin is rigid and cannot ring-flip, whereas cis-decalin can easily ring-flip.

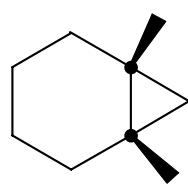


Solution: (a) In cis-decalin as shown in (a), to the ring 1, the bond a is an axial bond, and bond b is an equatorial one, when it ring-flip, bond a become an equatorial one, and bond b become an axial one, ring 2 also can formed. But to trans-decalin, the situation changed, both bond a and b are equatorial one, when ring-flip, they both become axial ones, then ring 2 cannot be formed. So trans-decalin is rigid and cannot ring-flip and cis-decalin can easily ring-flip.

4.49 trans-Decalin is more stable than its cis isomer, but cis-bicyclo[4.1.0]heptane is more stable than its trans isomer. Explain.

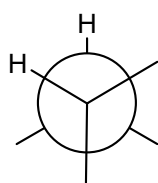
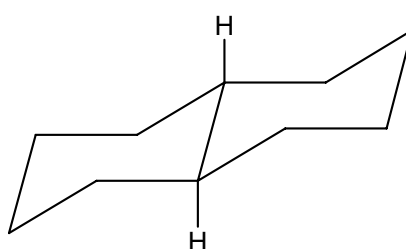
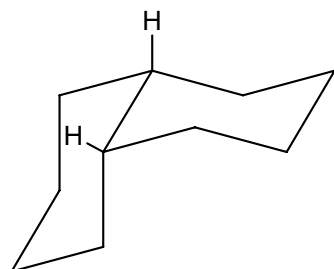


Trans-Decalin

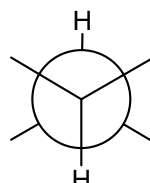


cis-Bicyclo[4.1.0]heptane

Solution:



cis-Decalin



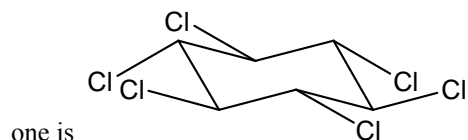
trans-Decalin

from the Newman project, it's clear that the trans-Decalin is more stable than its cis isomer. But for

cis-bicyclo[4.1.0]heptane and its trans isomer, it is hard for the adjacent trans bonds of cyclopropane to form cyclohexane because of its far distance.

4.50 How many cis-trans stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane are there? Draw the structure of the most stable isomer.

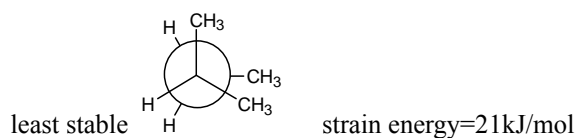
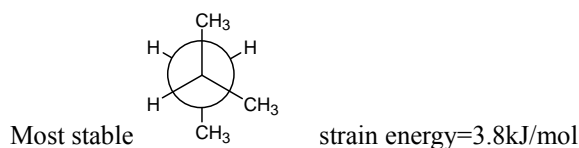
Solution: There are 8 cis-trans stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane. The most stable



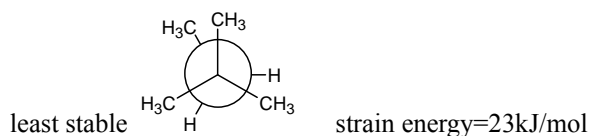
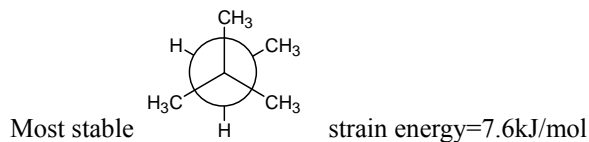
4.51 Sight along C2-C3 bond and draw Newman projections of the most and least stable conformations. Assign energy values.

Solution:

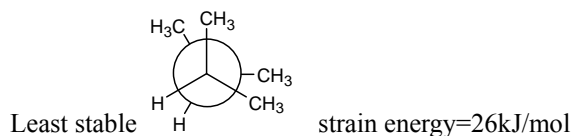
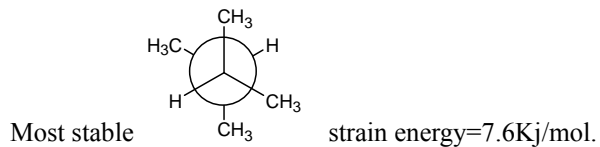
(a) 2-Methylbutane



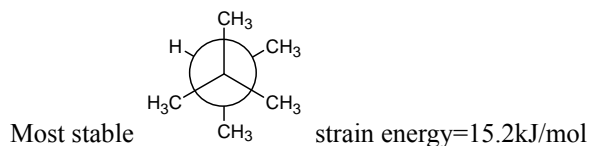
(b) 2,2-Dimethylbutane

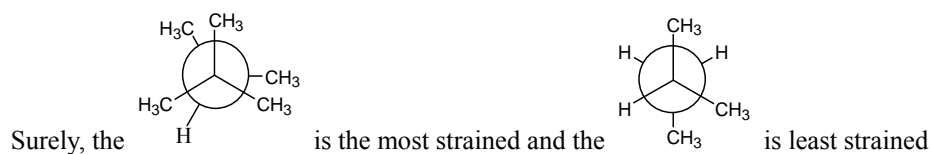
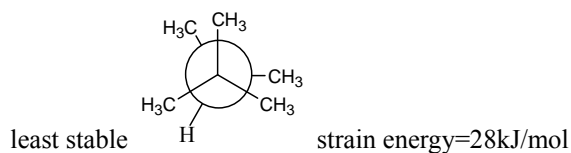


(c) 2,3-Dimethylbutane

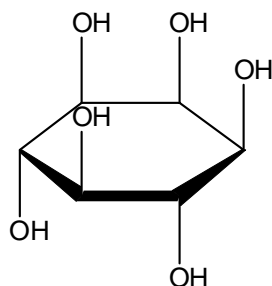


(d) 2,2,3-Trimethylbutane

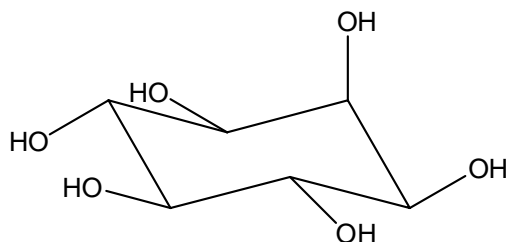




4.52 myo-Inositol, one of the isomers of 1,2,3,4,5,6-hexahydroxycyclohexane, acts as a growth factor in both animals and microorganisms. Draw the most stable chair conformation of myo-inositol.

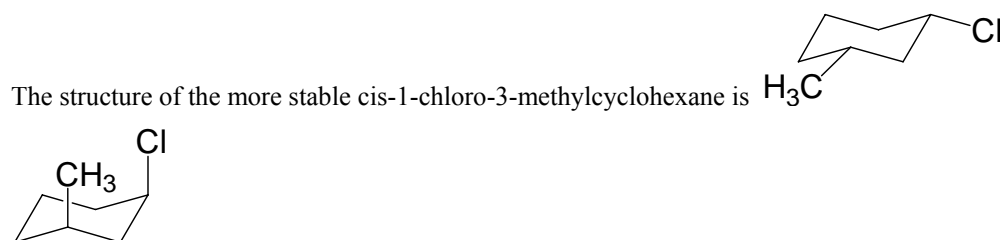


Solution:



4.53 One of the two chair structures of cis-1-chloro-3-methylcyclohexane is more stable than the other by 15.5 kJ/mol (3.7 kcal/mol). Which is it? What is the energy cost of a 1,3-diaxial interaction between a chlorine and a methyl group?

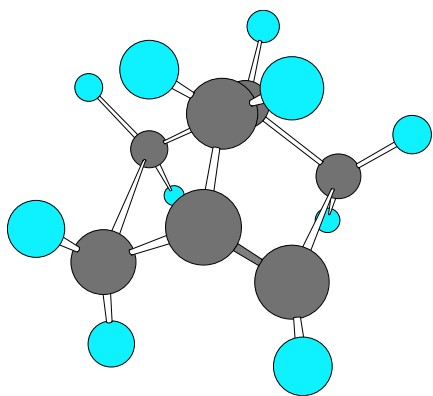
Solution:



$$15.5 \text{ kJ/mol} - 1.0 \text{ kJ/mol} - 3.8 \text{ kJ/mol} = 10.7 \text{ kJ/mol}$$

So the energy cost of a 1,3-diaxial interaction between a chlorine and a methyl group is 10.7 kJ/mol.

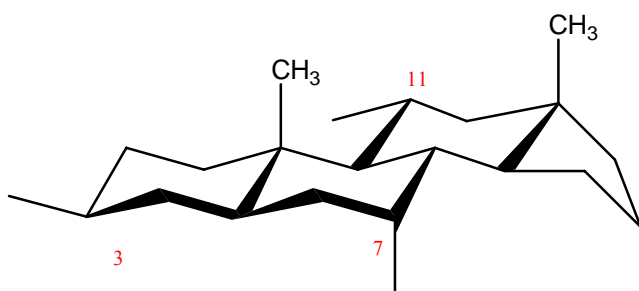
4.54 The German chemist J. Bredt proposed in 1935 that bicycloalkenes such as 1-norbornene, which have a double bond to the bridgehead carbon, are too strained to exist. Make a molecular model of 1-norbornene, and explain Bredt's proposal.



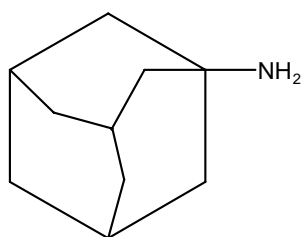
Solution: First, it may contain strong angle strain. For example, the carbon-carbon-carbon single bond which at the six-atom-ring is smaller than 109° and the carbon-carbon-carbon single bond which connect the bridgehead is also smaller than 109° . This caused strong angle strain. Second, it may contain strong torsional strain. The four hydrogen atom which is at the bottom of the molecular in the picture caused torsional strain.

4.55 Tell whether each of the following substituents on a steroid is axial or equatorial. (A substituents that is “up” is on the top face of the molecule as drawn, and a substituent that is “down” is on the bottom face.)

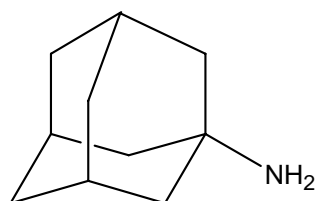
- (a) Substituent up at C3 equatorial
- (b) Substituent down at C7 axial
- (c) Substituent down at C11 axial



4.56 Amantadine is an antiviral agent that is active against influenza A infection. Draw a three-dimensional representation of amantadine showing the chair cyclohexane rings.

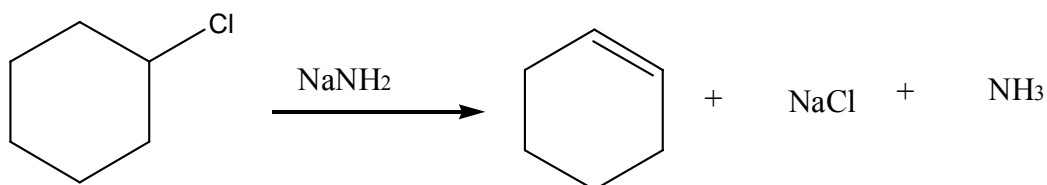


Solution:



4.57 Alkyl halides undergo an elimination reaction to yield alkenes on treatment with strong base. For

example, chlorocyclohexane gives cyclohexene on reaction with NaNH_2 :

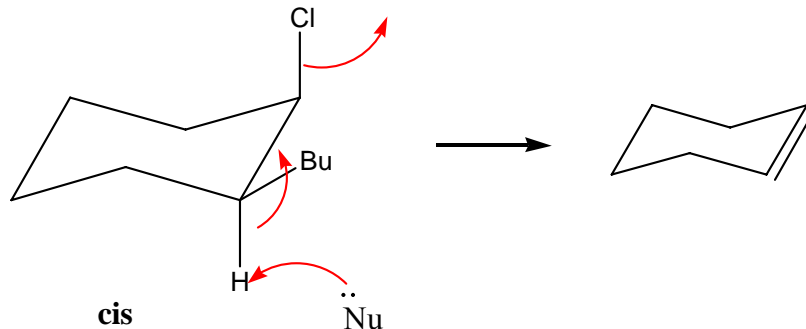


If axial chlorocyclohexanes are generally more reactive than their equatorial isomers, which do you think would react faster, cis-1-tert-butyl-2-chlorocyclohexane or trans-1-tert-butyl-2-chlorocyclohexane? Explain.

Solution:

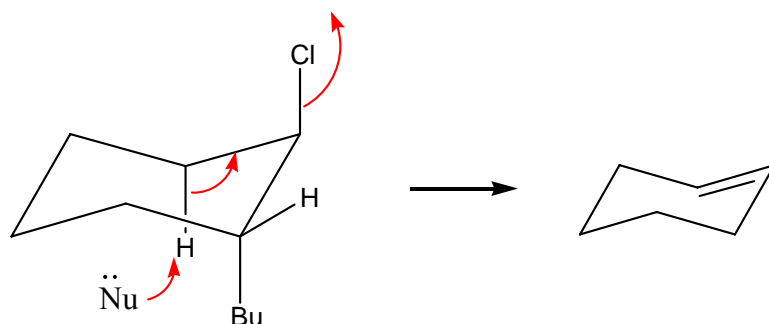
cis-1-tert-butyl-2-chlorocyclohexane will go reaction faster.

Because the cis one is staggered:



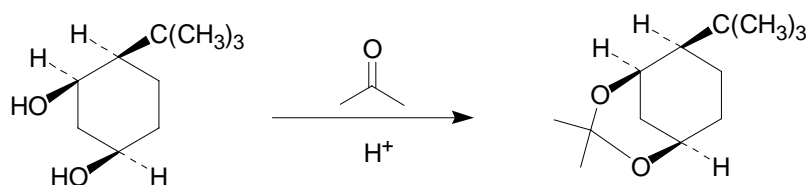
It's a Zaitsev product.

While the trans one is eclipsed at the Butyl side, so it should be eliminated on the other side, which forms a non-Zaitsev product.



So the cis one will react faster.

4.58 Ketones react with alcohols to yield products called acetals. Why does the all-cis isomer of 4-tert-butylcyclohexane-1,3-diol react readily with acetone and an acid catalyst to form an acetal. But other stereoisomers do not react? In formulating your answer, draw the more stable chair conformations of all four stereoisomers and the product acetal. Use molecular models for help.



Solution:

