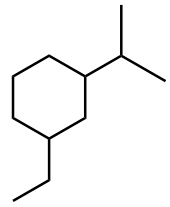
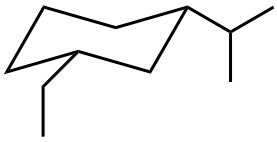
Tutorial 5

Q1. The following molecule has two diastereomers. Diastereomer **1** can assume a chair conformation lower in energy than any chair conformation of diastereomer **2**.



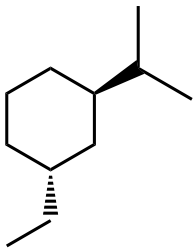
a) Draw diastereomer **1** in its lowest energy chair conformation.

Answer:

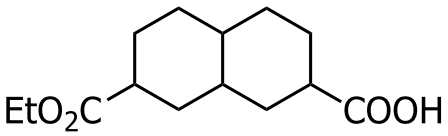


b) Draw the structure of diastereomer **2** (in 2-D). Clearly show any important stereochemistry.

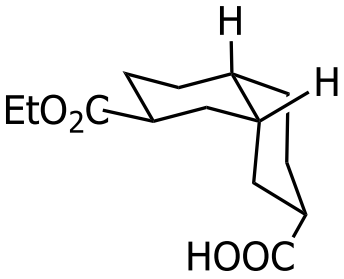
Answer:



Q2. Draw the 3-D structure of the molecule below wherein the ring junctions are cis- and both the substituents are in the equatorial position.

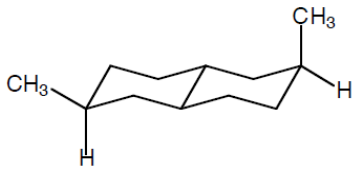


Answer 2.

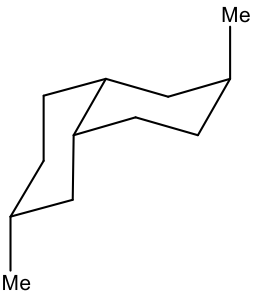


Q3. Draw the Newman projections for the following decalins.

a)

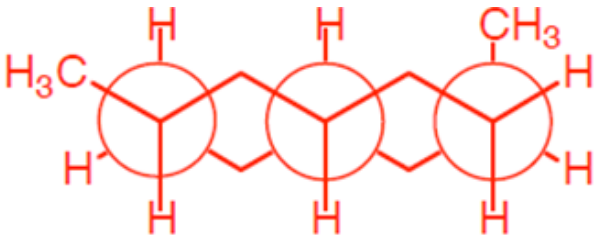


b)

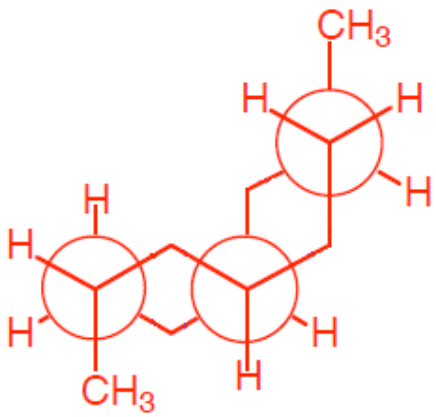


Answer:

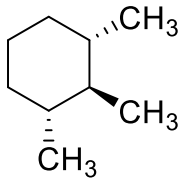
a)



b)

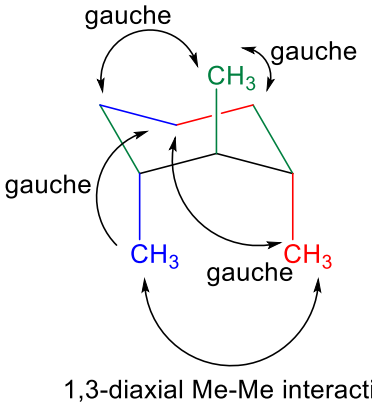


Q4. Consider the following trimethyl-substituted cyclohexane shown below. It can exist in two chair conformations that differ in energy by 4.4 kcal/mol. Draw the two possible chair conformations, note all the axial methyl groups and predict which one of the chair conformations is the most stable. In one of these conformations, there exists a 1,3-diaxial Me-Me interaction.

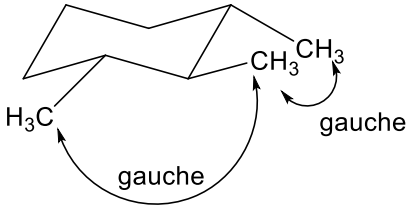


Calculate the energy corresponding to the 1,3-diaxial methyl-methyl interaction. It is given that the energy of Me-Me and Me-CH_2- gauche interactions are the same (0.9 kcal/mol).

Answer:



1,3-diaxial Me-Me interaction



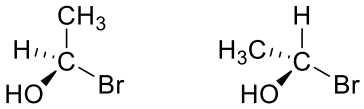
The chair with all methyls equatorial is most stable. The energy of the left chair is due to 4 gauche interactions and one 1,3-diaxial methyl-methyl interaction. The energy of the right chair has 2 gauche. So equating the two with the 4.4 kcal/mol energy difference gives

4 gauche + 1,3-diaxial = 2 gauche + 4.4 kcal/mol
4(0.9) + 1,3-diaxial = 2(0.9) + 4.4 kcal/mol
1,3-diaxial = 2.6 kcal/mol

Q5. Indicate whether the following pairs of compounds represent the same molecule, pairs of enantiomers, diastereomers, meso compounds, or stereochemically unrelated molecules.

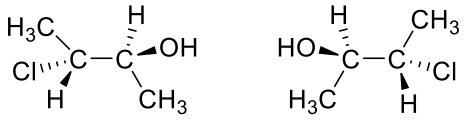
a) 

b) 

c) 

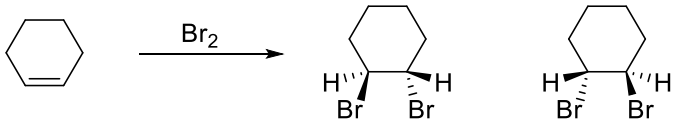
d) 

e) 

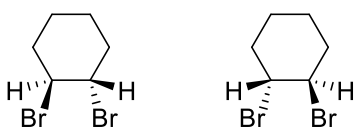
f) 

Answer:
a) Chiral molecule and its mirror image - enantiomers.
b) R-isomer on the left, S-isomer on the right - enantiomers.
c) -OH and -Br are in the same positions, but -H and -CH3 have been exchanged - enantiomers.
d) R-isomer on the left, R-isomer on the right - same molecule.
e) Both molecules are chiral, but they do not have the same groups attached to the chiral carbon - unrelated.
f) Each molecule is chiral (no plane of symmetry) and they are mirror images - enantiomers.

Q6. The bromination of cyclohexene gives the two compounds shown below. Assign R or S to each chiral center in the products. Are the two molecules enantiomers, diastereomers or identical?



Answer: The products are enantiomers.



S S **R R**

Q7. Given that (S)-bromobutane has a specific rotation of $+23.1^{o}$, what is the optical purity and % composition of a mixture whose specific rotation was found to be $+18.4^{o}$?

Answer:

The positive sign indicates that the (S)-isomer is in excess.

Optical purity, % = 100 [α]mixture / [α]pure sample
= 100 (+18.4) / +23.1o
= 80% this indicates a 80% excess of S over R!

The 20% leftover, which is optically inactive, must be equal amounts of both (R)- and (S)-bromobutane. The excess 80% is all S so there is a total of 10% (R) and 90% (S).