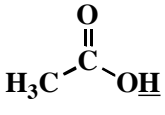
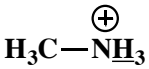
Homework 2
Organic Chemistry MCAT Review
Summer 2012
Brent Iverson

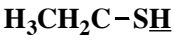
1. Complete the following two structures by adding appropriate numbers of lone pair electrons, H atoms, and formal charges to the atoms in the boxes. You must adjust your answers to indicate the predominant species at each indicated pH value. (You do not have to add anything such as H atoms to atoms not drawn in the boxes.) This problem is testing your understanding of the relationship of protonation state to pH to pKa values for certain functional groups we have discussed. Next, in the space provided, write the overall charge on each structure at the indicated pH. For your reference, here are the relevant pKa values:



$pK_a = 4.76$

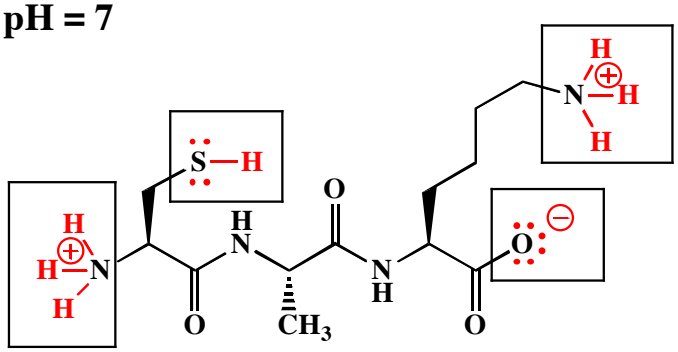


$pK_a = 10.64$



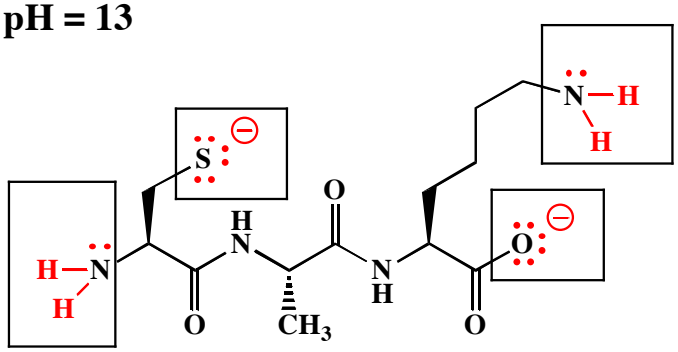
$pK_a = 10.6$

pH = 7



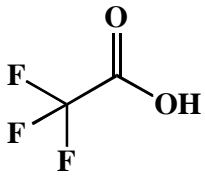
Total charge on molecule: +1

pH = 13

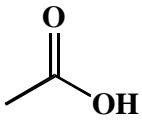


Total charge on molecule: -2

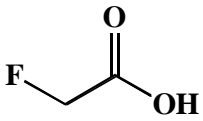
1 (cont.) Rank the following from weakest to strongest acid, with a 4 under the weakest acid and a1 under the strongest acid.



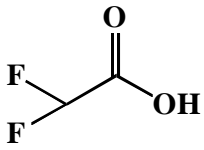
1



4

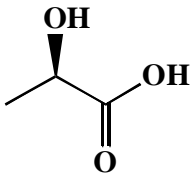


3



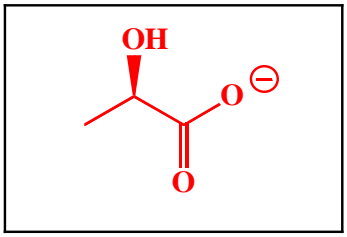
2

Consider the following acid that has two different pKa values as listed:

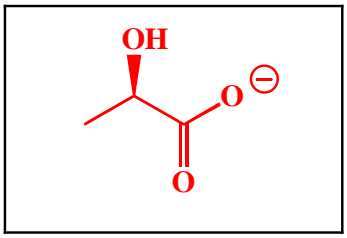


pKa = 3.08, 18.5

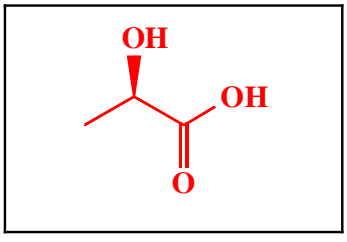
In the space provided, draw the predominant form of this acid in water at pH 10.0



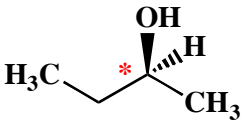
In the space provided, draw the predominant form of this acid in water at pH 7.0

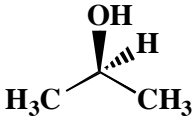


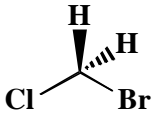
In the space provided, draw the predominant form of this acid in water at pH 1.0

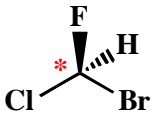


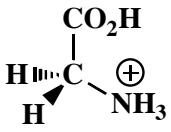
2. For the following molecules, label each chiral center with an asterisk (*).

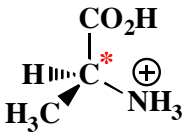


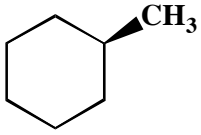


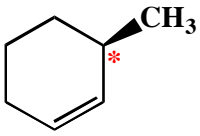


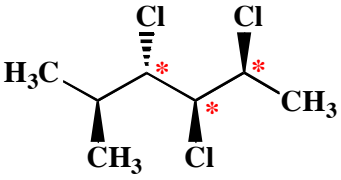


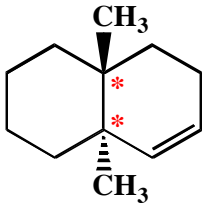


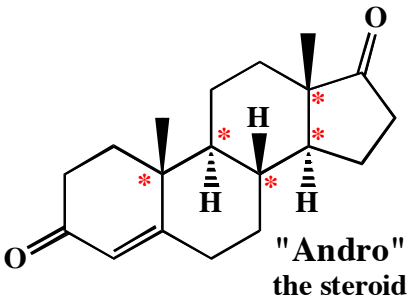






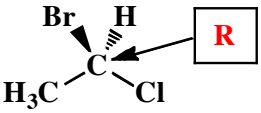


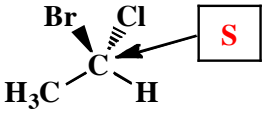


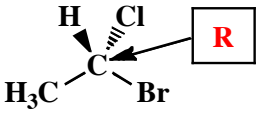


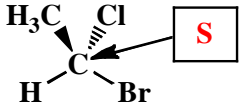
"Andro"
the steroid used by Mark McGwire and other sports stars

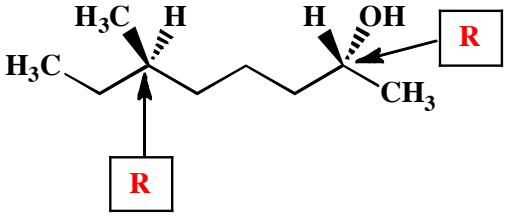
3. Label each chiral center as "R" or "S".

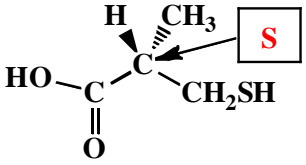






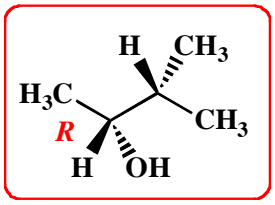


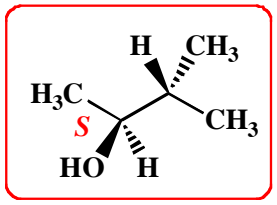




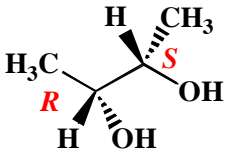
4. For each pair of molecules, on the line provided state whether they are (1) **enantiomers**, (2) **diastereomers**, (3) **consitutional isomers**,or (4) **different conformations of the same molecule.** Each pair of molecules will best be described by one of these four terms. **Nrxt draw a circle around all the molecules that would be optically active (i.e rotate the plane of plane polarized light), and write "MESO" under any meso compounds.**

Relationship:

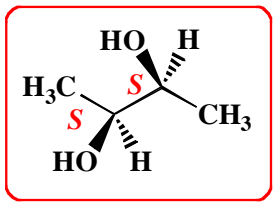




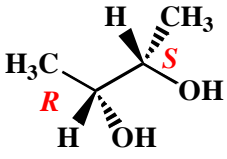
enantiomers



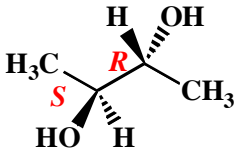
MESO



diastereomers

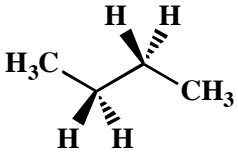


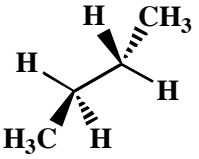
MESO



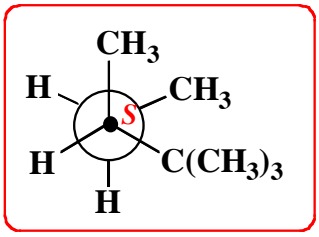
MESO

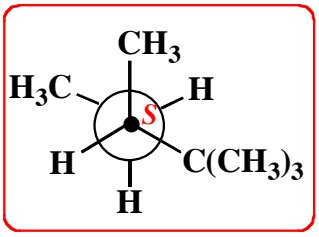
same molecule



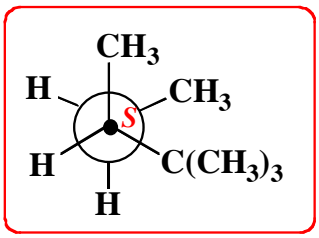


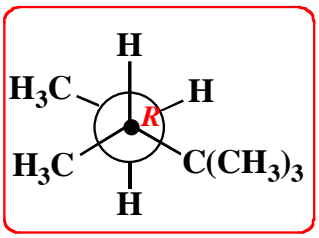
different conformations of the same molecule





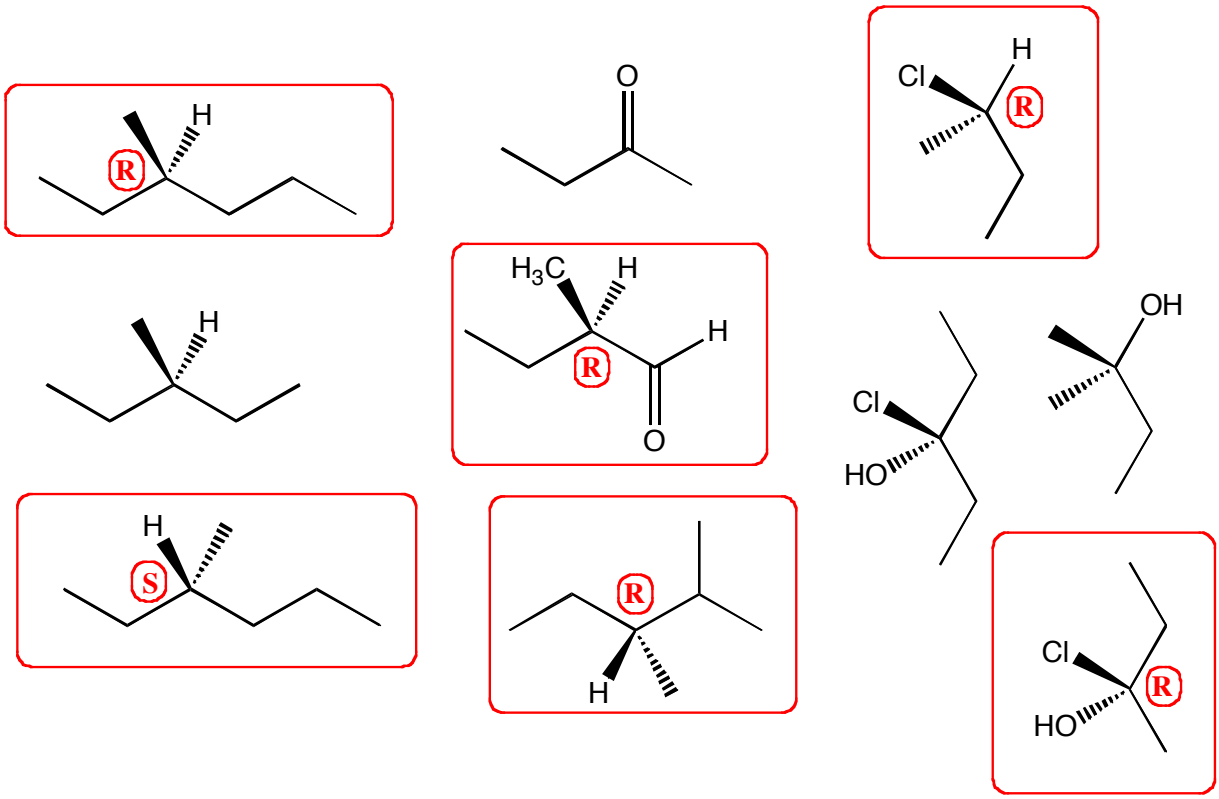
different conformations of the same molecule



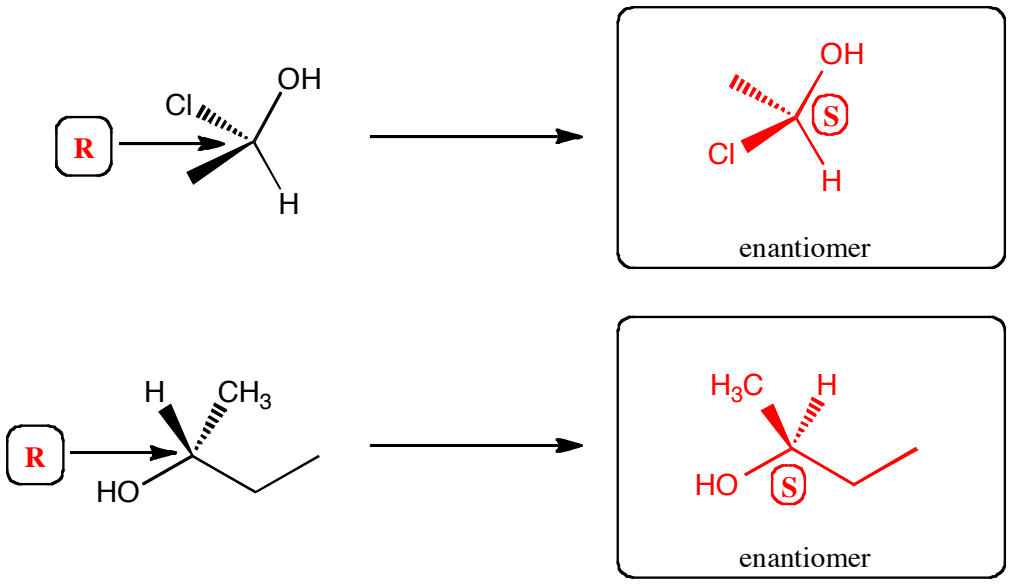


enantiomers

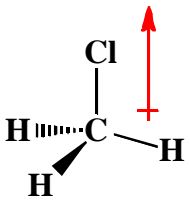
5. Circle the molecules that are chiral. For each one that is, determine the configuration of the chiral center and write "R" or "S" next to the chiral center.

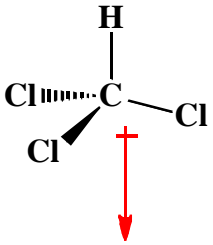


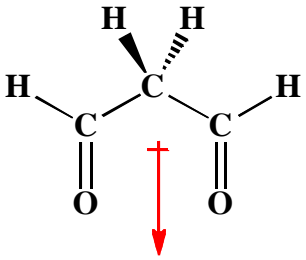
6. For each molecule, label the chiral centers as "R" or "S". Then, in the space provided to the right of each molecule, draw its enantiomer.

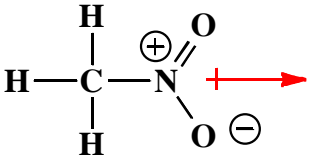


7. For the following molecules, use the dipole moment symbol ⟶ to show the direction of the molecular dipole moment in all molecules that have an overall molecular dipole.



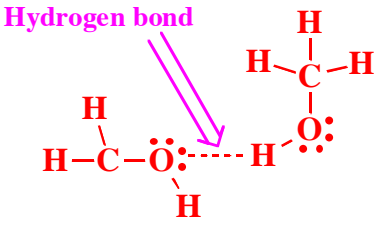




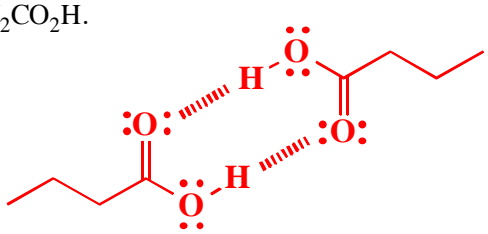


For the molecule above list the molecular dipole for the conformation shown.

8. A hydrogen bond is the strongest interaction seen among neutral molecules. In the space provided, draw two molecules of methanol (CH_3OH) and show a hydrogen bond between them. Use a dashed line to indicate the hydrogen bond. Show all lone pairs.



Carboxylic acids exist in solution as characteristic "dimers". Draw the structure of the dimer formed by butanoic acid, $CH_3CH_2CH_2CO_2H$.



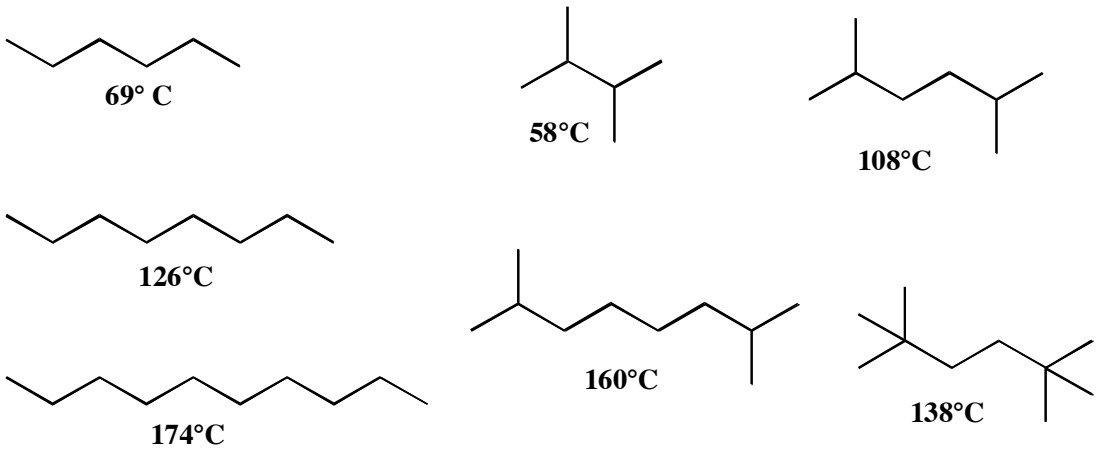
A Hydrogen-bonded dimer

9. Rank the following in order of boiling point, with a **1** under the molecule with the lowest boiling point and a **4** under the molecule with the highest boiling point.

$CH_3CH_2CH_2Cl$	$CH_3CH_2CH_2CH_3$	$CH_3CH_2CH_2OH$	CH_2OHCH_2OH
2 (46°C)	**1** (-0.5°C)	**3** (97°C)	**4** (197°C)

The stronger the attraction between molecules, the higher the boiling point. 1-chloropropane has a significant dipole moment allowing for dipole-dipole interactions, and the OH groups of the third and foutth molecules take part in hydrogen bonding, the strongest intermolecular interaction.

10. A series of alkanes are listed along with their boiling points.

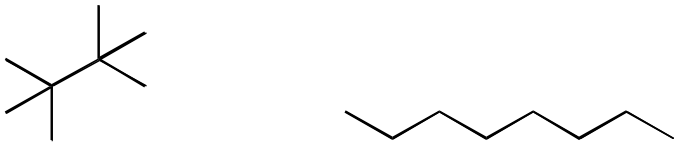


A) From the data listed, draw two different conclusions regarding how boiling point changes with structure.

Boiling Point increases with molecular weight. It takes more energy for molecules of greater mass to enter the gaseous state, and higher molecular weight also means greater surface area so stronger attraction to other molecules in the liquid state

Boiling point decreases with branching. As explained in class, this is due to a decrease in surface area for the branched alkanes, limiting total attraction via dispersion forces.

B) The boiling point of 2,2,3,3-tetramethylbutane is 106°C, in line with the other alkanes. However, 2,2,3,3-tetramethylbutane is a solid at room tempterature, not a liquid like the others, because it has a melting point of 104°C. It is only a liquid for the span of 2°C!! For comparison, octane is only a solid below -57°C. Briefly explain why 2,2,3,3-tetramethylbutane exhibits this unsual behavior.

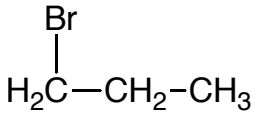


Boiling point 106°C
Melting Point 104°C

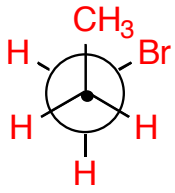
Boiling point 126°C
Melting Point -57°C

Even when 2,2,3,3-tetramethylbutane rotates about its central bond, it maintains a compact oval shape. Thus, individual molecules can pack well against each other and a solid is formed even at temperatures in which bond vibrations and rotations are occuring. On the other hand, when the interior bonds of octane rotate, the molecule takes on a highly irregular shape, incompatible with packing into a solid. Therefore, octane will only be a solid at temperatures so low that bond rotations are "frozen" out.

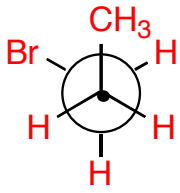
11. The following molecule is called 1-bromopropane. On the templates provided, draw both gauche conformations, as well as the anti conformations. Circle the most stable conformation of 1-bromopropane.



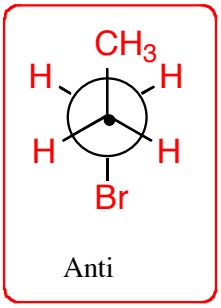
1-bromopropane



Gauche



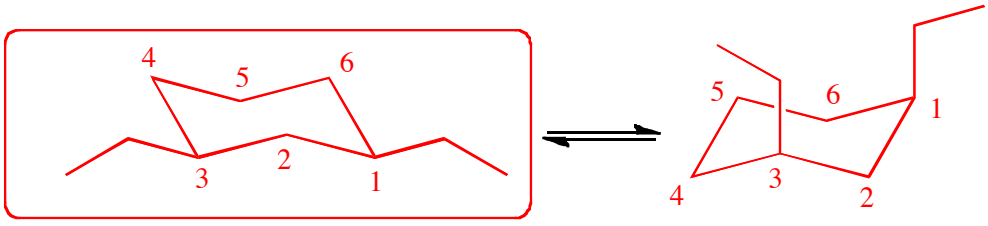
Gauche



Anti

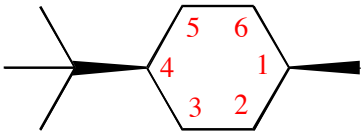
All three of the above conformations are examples of a staggered conformation

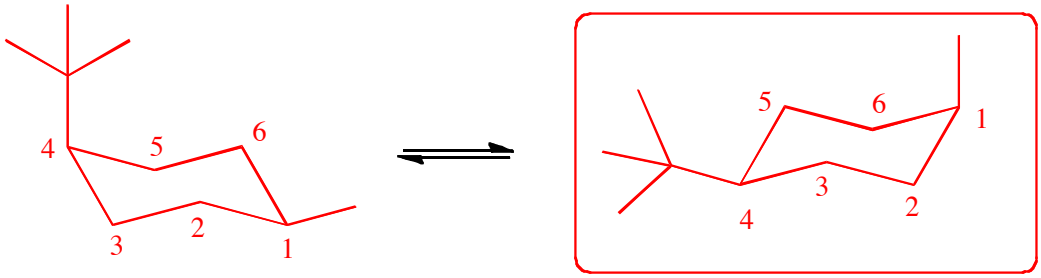
12. Draw the alternative chair conformations of *cis*-1,3-diethylcyclohexane. Draw a cicle around that is more stable, i.e. the one that predominates at equilibrium.



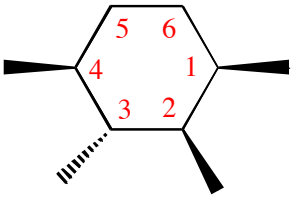
Both ethyl groups equatorial

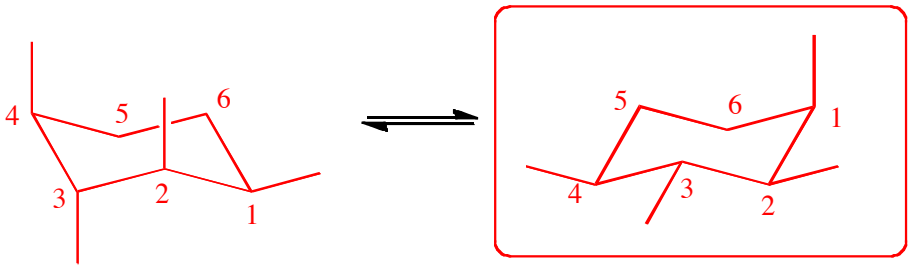
13. Draw the alternative chair conformations of the following cyclohexane derivatives. When there is a difference in energy, circle the more stable chair conformation (i.e. the one that predominates at equilibrium).





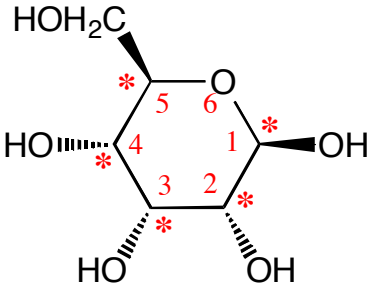
The larger *tert*-butyl group is equatorial in the more stable chair

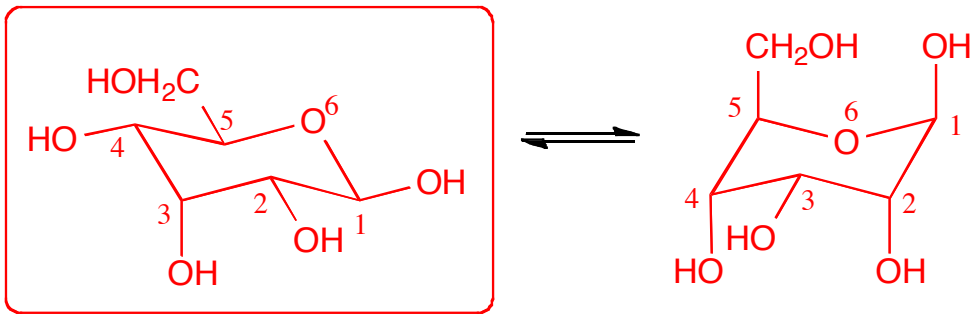


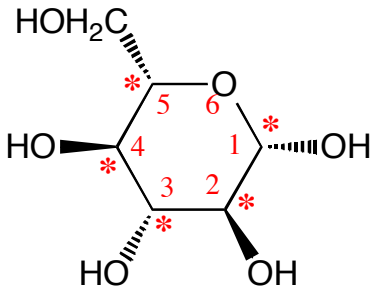


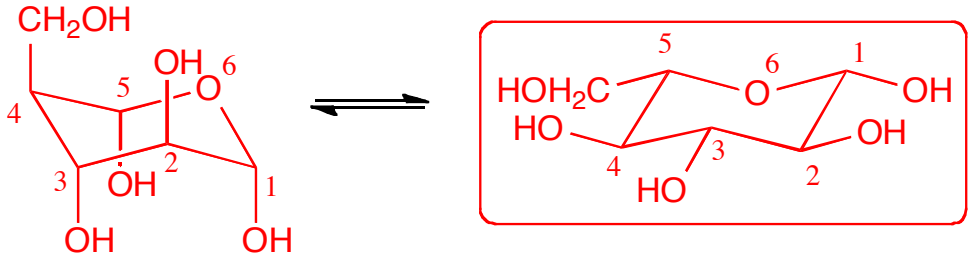
This chair has two equatorial methyl groups (on ring atoms 1 and 3) while the other chair only has a single equatorial methyl group.

13. First place an asterick next to each chiral center. Next draw the alternative chair conformations of the following carbohydrate derivatives. When there is a difference in energy, circle the more stable chair conformation (i.e. the one that predominates at equilibrium).









Are the above two carbohydrates the same molecule, enantiomers or diastereomers ?

They are diastereomers