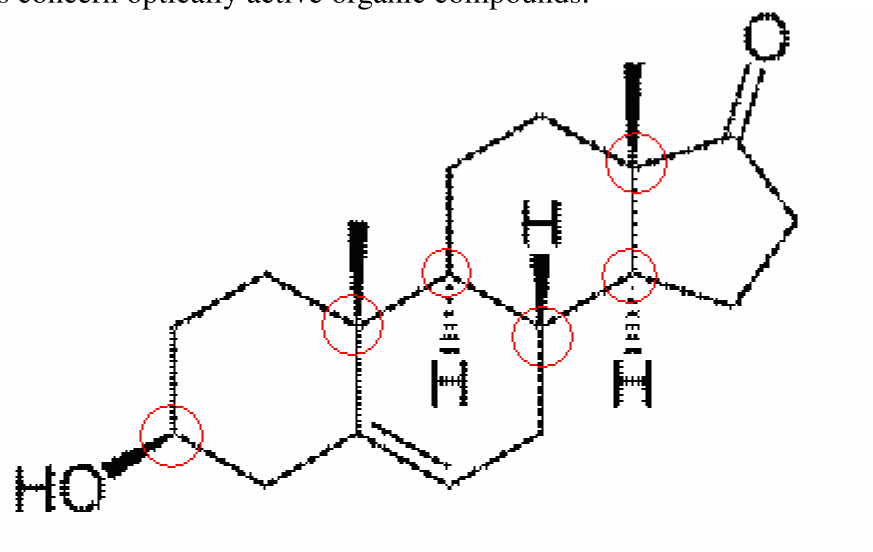
Name ____________________________

CHEM 230 SEMESTER 01-2015 HOMEWORK 4

Print out this homework on letter sized paper. Answer the questions carefully (not on this sheet) and then submit your answers on Monday morning at the start of class. Note that if there is clear evidence of copying, the whole exercise may attract a zero mark, and the matter may be reported to the authorities.

The following questions concern optically active organic compounds.



(The chiral centres are carbon atoms which have four different groups attached to them.)

1) Identify all the chiral centres in the above structure of dehydroepiandrosterone (DHEA) by circling the relevant carbon atoms. (3)

2) What is meant by the term *optically active*? (2)

An optically active compound is one which rotates the plane of polarisation of plane-polarised light.

3) What is meant by the term *racemic mixture*? (2)

A racemic mixture is one which consists of equal proportions of a pair of enantiomers and hence is not optically active.

4) What essential feature makes a compound optically active? (2)

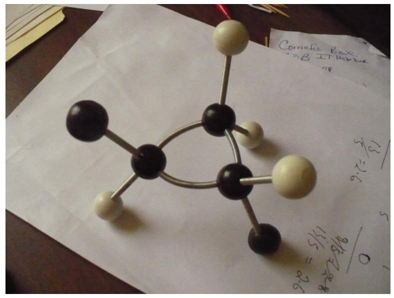
An optically active compound is chiral, that is, a molecule of it is not superposable on its mirror image.

5) Optically active compounds come in pairs of isomers. What term is used to designate these pairs of optical isomers? (1)

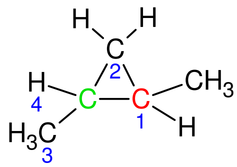
These are described as enantiomers.

6) The formula C_5H_{10} describes several different isomers, two of which are a pair of optical isomers. Give the stereochemical formula of each member of the pair and name them. Include the stereochemical designation (R or S) in the names. (Hint: they contain a ring.) (4)

To answer this question, it is advisable to build a model:

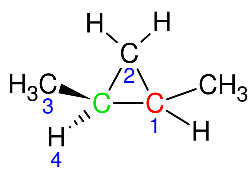


You can do this with Playdo, or, if you don't want to spend so much money, flour dough, or even just toothpicks and superglue. The model above represents 1,2-dimethylcyclopropane:

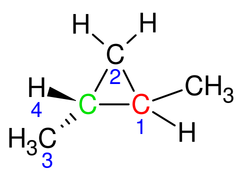


In order to answer this question properly, it is essential to recognise that there are two chiral centres, shown in green and red on the diagram above. Each chiral carbon has four different groups attached. Considering the green carbon (on the left), the group of highest priority attached to this carbon is labelled 1. It consists of a carbon atom (red) attached to two further carbons. The next highest priority carbon, labelled 2, has only one further carbon attached to it (the red one). Number 3 has only hydrogens attached to it, and number four, the lowest priority group, is a single hydrogen atom.

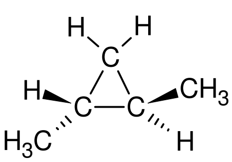
Placing the hydrogen at the back of the molecule and the methyl group in front, gives an (S) configuration about the green carbon since counting 1,2,3 gives an anticlockwise rotation.



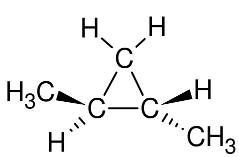
Changing the places of groups 3 and 4 necessarily changes the configuration from (S) to (R).



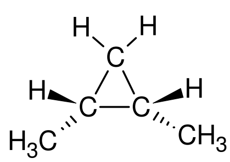
Repeating the procedure with the red carbon gives three isomers:



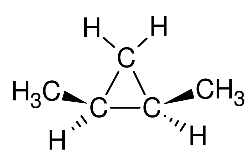
(1R,2R)-



(1S,2S)-



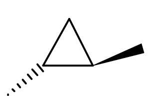
(1R,2S)-



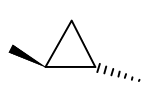
(1S,2R)-1,2-dimethylcylopropane

Although four structures are given above, a little consideration will show that the (1R,2S) and (1S,2R) structures are in fact the same – it's easy if you build models! These represent a *meso* compound (which may also be called *cis*-1,2-dimethylcyclopropane) since there is a plane of symmetry in the molecule.

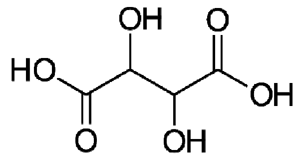
The simplest way to represent the enantiomers is as shown below:



and



These two diagrams, together with the names: (1R,2R)-1,2-dimethylcylopropane and (1S,2S)-1,2-dimethylcylopropane, would attract full marks.

7) Tartaric acid (2,3-dihydroxybutanedioic acid):  has two chiral centres and three stereoisomers, designated as (2R, 3R)-tartaric acid, (2S, 3S)-tartaric acid and (2R, 3S)-tartaric acid.

a) How are (2R, 3R)-tartaric acid and (2S, 3S)-tartaric acid related to one another? (1)

These are enantiomers of one another.

b) How are (2R, 3R)-tartaric acid and (2R, 3S)-tartaric acid related to one another? (1)

These are diastereomers of one another.

c) The names (2S, 3R)-tartaric acid and (2R, 3S)-tartaric acid describe mirror images which are identical, a *meso* compound. What feature distinguishes such compounds? (1)

Such compounds consist of molecules which possess a plane of symmetry.

d) What is the specific rotation, $[\alpha]_D^{20}$, of (2S, 3R)-tartaric acid? (1)

Since this compound is *meso* it is not optically active, and so the answer is zero ml g^{-1} dm^{-1}

e) What is the specific rotation, $[\alpha]_D^{20}$, of racemic tartaric acid? (1)

Again zero ml g^{-1} dm^{-1}.

f) What is the specific rotation $[\alpha]_D^{20}$, of (2R, 3R)-tartaric acid, given that the value for (2S, 3S)-tartaric acid is -12.4°ml g^{-1} dm^{-1}? (1)

The specific rotation is just the negative of its enantiomer, (2S, 3S)-tartaric acid is -12.4°ml g^{-1} dm^{-1}, +12.4°ml g^{-1} dm^{-1}

8) a) Calculate the optical purity of a sample of 2-bromobutane that shows a value of $[\alpha]_D^{20}$ = 12.4°ml g^{-1} dm^{-1}, given that $[\alpha]_D^{20}$ for (2S)-2-bromobutane is 23.1°ml g^{-1} dm^{-1}. (2)

Optical purity (or enantiomeric excess) is given by

$$\frac{\{[\alpha]_D^{20}\}_{mix}}{\{[\alpha]_D^{20}\}_{pure}} = \frac{12.4}{23.1} = 0.536797... \approx \underline{\underline{53.7\% \text{ to 3 sig. figs.}}}$$

b) Calculate the proportion of (2R)-2-bromobutane in the mixture. (2)

53.7% represents the proportion of the mixture by which the (2S)-2-bromobutane is in excess over the racemic mixture, since the specific rotation of both the mixture and this enantiomer are both positive. Hence 100 – 53.7 = 46.3% of the mixture consists of equal amounts of the (2R)-2-bromobutane and the (2S)-2-bromobutane. Hence half of this 46.3% (= 23.15%) is (2S)-2-bromobutane and the other half (2R)-2-bromobutane, so the total percentage of (2R)-2-bromobutane is 23.15% ~23.2% to 3 sig. figs.