NOMENCLATURE OF STEREOISOMERS

A. <u>Determining the Priority of the Atoms</u>

- Priority is established by three criteria, applied in order until a difference is found.
 a) Higher atomic number precedes lower.
 - b) Higher atomic weight precedes lower.
 - c) Multiple bonded atoms are treated by counting the doubly bonded atom twice (thrice) at *both* ends of the multiple bond.
- 2. If there is more than one atom of identical priority (usually C) attached to the chiral center, the priority of the atoms is determined by what is attached to them in the following way (called *the sequence rules*):
 - a) Compare the first atom of each side chain attached to the chiral center. If they have identical priority. . .
 - b) Compare the highest priority atoms attached to that first atom, then the second highest priority atom, then the third, using the priority rules in 1.
 - c) If two or more atoms still have identical priority, continue out the chain one atom at a time, looking at highest priority atoms first, as described in b), until a difference is found. See example on page 2.

B. <u>Chiral Centers, R or S Configuration</u>

- 1. Pick out the chiral centers. For each, determine the priority order of the attached atoms (determined by the rules in A).
- 2. Place the molecule in such a position that the atom / group of lowest priority (frequently H) is behind the chiral carbon from your viewing position. Trace a path from the group of highest priority to the second and then the third. If the path followed is clockwise, the configuration is called R (rectus); if counterclockwise, S (sinister).
- 3. The configuration names are placed in parentheses in front of the IUPAC name as follows: *(2R, 3S)*-2-chloro-3-methylhexane.
- 4. <u>Informal Terms</u>. *d* and *l* (*dextro* and *laevo*) refer to positive or negative rotation of plane polarized light and give no information about configuration; the *correct* designations of the directions of measured optical rotations are (+) and (-). *D* and *L* refer to same or opposite configuration compared to *d*-glyceraldehyde and should only be used for sugars.

C. <u>Double Bonds, E or Z Configuration</u>

- 1. Identify the atom of highest priority on each carbon of the double bond (see A).
- 2. If the two groups of highest priority are on the same side of the double bond, the configuration is **Z** ("zusammen"); if on opposite sides, **E** ("entgegen").
- 3. <u>Informal Terms</u>. *Cis* and *trans* (and less often *syn* and *anti*) are used to describe whether two groups you have identified are on the same or opposite sides.

Some advice: If you remember that we are trying to give a priorities to the atoms attached to the individual chiral element (center or double bond) by examining what is attached, rather than prioritizing the whole group that is attached, you are less likely to make mistakes by comparing the wrong things and less likely to be confused if there is more than one chiral center. Examine the attached atoms one level at a time - don t try to prioritize by glancing at the whole group.

Do not try to redraw a structure to determine its configuration - even experts make

mistakes doing that. Don t be shy about writing on the sketch. **Complex Example of Determining the Priorities** (Fischer projection):



1. Compare first atoms out: C = C = C > H.

2. For those first atoms (C) that are equal, compare *second* atoms out, selecting the *highest* priority atom attached to each of the first atoms; these are labeled \Box . C = C > H: C₂ is still indistinguishable from C₄, but both have higher priority than the methyl C.

3. To distinguish C_2 and C_4 , examine the second atoms of *2nd highest* priority. To do that, redraw the double bond showing each carbon of the double bond as if it occurred twice; these

atoms are labeled \triangle . $C = C: C_2$ and C_4 are still not distinguished. 4. Then, compare second atoms out of *3rd highest* priority,

labeled ∇ . H = H: all the second atoms out are the same for C₂ and C₄ and they are not distinguished.

- 5. Compare the *third* atoms out, beginning with the highest priority third atom attached to the highest priority *second* atom, labeled \diamond . C > H: C₂ has a higher priority than C₄.
- 6. Therefore, priorities are: $C_2 > C_4 > CH_3 > H$. Remember in a Fischer projection the vertical bonds are curled back. The configuration is **S**. The full name is **(S)**-3,4-dimethyl-1-pentene.

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