1. Define "stereogenic center". What is the difference between a chiral center and a stereogenic center?

   A stereogenic center is an element where the interchange of two substituents will lead to a stereoisomer. A chiral center is a specific type of stereogenic center where reflection of the molecule results in a non-superimposable mirror image of that center.

2. Define the terms "stereoselective reaction" and "stereospecific reaction" and give an example of each.

   A "stereoselective reaction" results in the preferential formation of one stereoisomer over the other possible stereoisomers. A reaction is stereospecific if the starting materials are converted specifically to distinct stereoisomers depending on the starting configuration.

   ![Stereoselective reaction example](image)

   Stereospecific reaction-- only trans product observed

   ![Stereoselective reaction example](image)

   Stereoselective reaction-- the exo epoxide is preferred

3. Define the terms "diastereotopic face" and "enantiotopic face" and give an example of each.

   If addition of a ligand to either face of a double bond will result in a pair of diastereomers, the faces are diastereotopic. If addition of a ligand to either face of a double bond will result in a pair of enantiomers, the faces are enantiotopic.

4. Why is the following title nonsensical? "A Chiral Total Synthesis of Strychnine"

   Chiral is an adjective meaning "not superimposable with its mirror image"; as such it can only be applied to physical objects.
5. Define "allylic strain". Give an example of a molecule with A^{1,2} strain and one with A^{1,3} strain.

Allylic strain is the comparatively increased repulsive non-bonded interactions between medium or large groups held near to each other by the presence of sp^2 hybridized atoms.

6. Why will we discuss the products of reactions in terms of "enantiomeric purity" rather than "optical purity" in 5.512?

Enantiomeric purity is a measure of the ratio of the enantiomers present in a sample. Optical purity instead refers to the ratio of the optical rotation of a sample containing enantiomers to the optical rotation of a pure sample of a single enantiomer. Optical purity does not always correlate directly to the ratio of the enantiomers present in a sample. In addition, optical rotation can be difficult to measure accurately due to the presence of trace impurities with large rotations, and the optical rotation of enantiomerically pure compound is not always known precisely.

7. Define "kinetic resolution".

Kinetic resolution is the separation of a single enantiomer from a racemic mixture by reaction of the mixture with a sub-stoichiometric amount of chiral reagent that reacts faster with and consumes the undesired enantiomer.

8. Define "antiperiplanar" and "synclinal" and illustrate each using both Newman projections and sawhorse representations for n-butane.

Two groups are synclinal if they are attached to adjacent, bound atoms and the angle formed by the groups when viewed along the axis of the bound atoms is approximately 60 degrees. Two groups are antiperiplanar if they are attached to adjacent, bound atoms and the angle formed is approximately 180 degrees.

9. Define "prochiral faces" and illustrate with an example.

If the addition of a group to a face of a double bond in an achiral molecule would lead to a product that is chiral, that face is prochiral.
10. What is the barrier to rotation (in kcal/mol) about the carbon-carbon bond in ethane?
2.9 kcal/mol

11. Draw the s-cis and s-trans conformations of acrolein. Which is lower in energy?

\[ \text{s-cis} \quad \text{s-trans} \quad \text{s-trans is more stable by 1.7 kcal/mol} \]

12. Rank the following substituents in term of conformation free energies on cyclohexane rings: CH₃, OH, CN, OMe, ethynyl, i-Pr, CHO, Br, CO₂Et, H.

\[ \text{H < CN < ethynyl < OH ~ OMe ~ CHO ~ Br < CO₂Et < Me < i-Pr} \]

13. Define the "anomeric effect" and provide an example.

The anomeric effect is the preference for synclinal isomers in fragments of type Y-C-X-C where Y and X are heteroatoms with at least one being O, N, or F possessing a lone pair of electrons. It is generally attributed to stabilization resulting from donation of an electron density from an adjacent antiperiplanar lone pair into the \( \sigma^* \) orbital of a carbon-heteroatom bond.


\[ \text{trans-decalin} \]

15. Draw the cis and trans conformational isomers of methyl acetate. Which is lower in energy? By how much?

\[ \text{trans} \quad \text{cis} \quad \text{The trans isomer is lower by 8.5 kcal/mol} \]