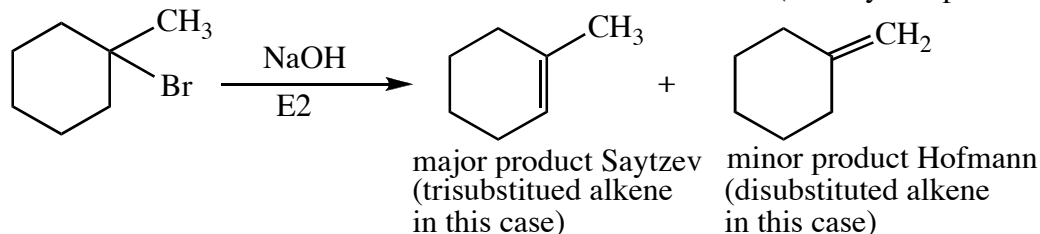


Regiochemistry And Stereochemistry

I. Regiochemistry or regioselectivity refers to what region or area of two possible and similar regions will be involved in a reaction. For example, in an elimination reaction of 1-bromo-1-methylcyclohexane with sodium hydroxide, regioselectivity is the favoring of elimination between the carbons that would result in the more substituted alkene (the Saytzev product).



General Examples where regiochemistry can be observed:

- Saytzev vs Hofmann elimination. (Chapter 11)
- Markovnikov vs. AntiMarkovnikov Addition (Chapter 12)
- Ortho/para vs meta substitution (Chapter 15)
- Baeyer-Villiger Reaction (Chapter 17: Which carbon migrates?)

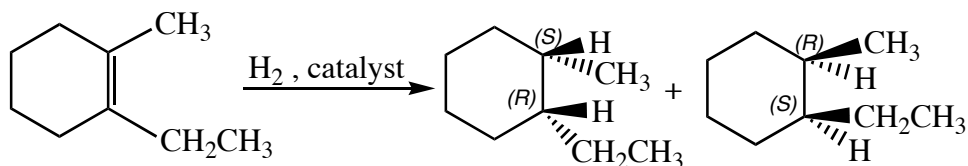
II. Stereochemistry could refer to **stereoselectivity** or **stereospecificity**.

A. Stereoselectivity: When one stereoisomer forms predominantly over other stereoisomeric possibilities. Elimination (E2, anti-periplanar) is stereoselective in making more *trans* than *cis* alkene products. Ex: Add ethoxide to 2-bromobutane. You get 3 products: mostly *trans*-2-butene, but also *cis*-2-butene and 1-butene (Chapter 11). (Geometric (*cis/trans*) isomers are considered to be stereoisomers, but they are achiral stereoisomers because the two forms are not mirror images of each other; they are in fact a type of diastereomers.)

B. Stereospecificity: When one stereoisomer forms exclusively rather than other stereoisomers. For example, Addition to a double bond may be *syn* (*cis*) addition, as with Example 1 below, or it may be *anti* (*trans*) addition, as with Example 2 below.

Examples of a **stereospecific** reaction:

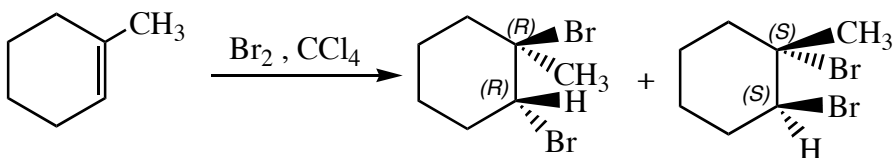
Example 1. *Syn* addition of H₂ to an alkene. (Chapter 12)



Note that the hydrogens are on the same side of the ring. (You do not need to determine the absolute configurations in this particular problem to see the *syn* addition; I only show configurations to emphasize to you that the two enantiomers are not the same, that is, the hydrogens will add *syn* in

two different ways depending on whether they happened to add to one side or the other side of the 1-methylcyclohexene.)

Example 2. Anti addition of HX to an alkene. (Chapter 12)



Note that the bromine atoms add anti to each other. (You do not need to determine the absolute configurations in this particular problem to see the anti addition; I only show configurations to emphasize to you that the two enantiomers are not the same, that is, the bromines will add anti in two different ways depending on whether the intermediate bridge happened to form on one side or the other of the cyclohexene.)