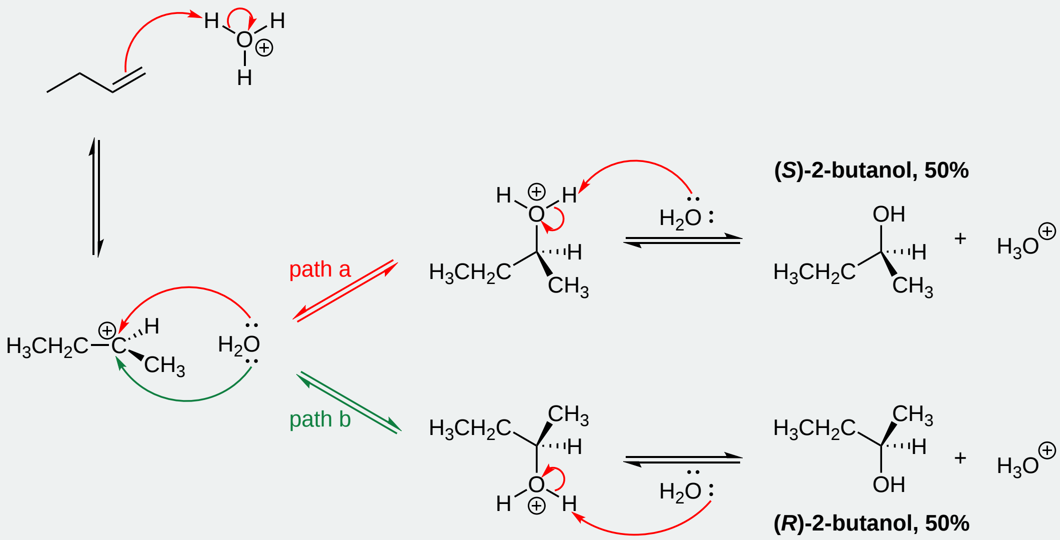
8.12: STEREOCHEMISTRY OF REACTIONS - ADDITION OF H₂O TO AN ACHIRAL ALKENE

OBJECTIVE

After completing this section, you should be able to account for the stereochemistry of the product of the addition of water to an alkene in terms of the formation of a planar carbocation.

STUDY NOTES

Organic reactions in the laboratory or in living systems can produce chiral centres. Consider reaction of 1-butene with water (acid catalyzed). Markovnikov regiochemistry occurs and the OH adds to the second carbon. However, both (*R*) and (*S*) products occur giving a racemic (50/50) mixture of 2-butanol. How does this occur? The proton addition to 1-butene results in a planar carbocation intermediate. A molecule of water is then equally likely to attack from the top (path a) or the bottom (path b) of this cation to produce either (*S*)-2-butanol or (*R*)-2-butanol, respectively.



As a reminder, a chiral center is a carbon that is bonded to four different groups. Organic reactions whether taking place in the body or in the laboratory can result in the product having a chiral center. The example in the study notes uses 1-butene to yield a product that contains a carbon with four different groups attached. Does this mean we get just one stereoisomer? Do we get a mixture of enantiomers? What is the stereochemistry of the reaction?

The product formed from 1-butene acid-catalyzed hydration reaction is a racemic mixture of 2-butanol. So, both R and S enantiomers are present. For more clarity, we can look into the mechanism for this reaction. The first step protonates 1-butene to yield a carbocation. The carbocation has an sp^2-hybridized carbon in a trigonal planar geometry. The planarity of the carbocation allows the nucleophlic water to attack from either side of the plane equally. Many refer to this as top and bottom attack.

One thing to consider is you cannot create chirality from something that is achiral. 1-butene is achiral as is the carbocation intermediate. Therefore, our product must also be achiral and to do this with a molecule that does contain a chiral center means that both enantiomers must be present. In other words, the product is formed as a racemic mixture. While this may be true in the laboratory, biological reactions can give a single enantiomeric product. This is because the enzyme catalyzing the reaction itself is chiral and can therefore yield a chiral product. An example of this is *cis*-aconitate, which is achiral, to (2R,3S)-isocitrate, which is chiral. In this case, aconitase is the enzyme that holds the *cis*-actonitate in a chiral environment, which does create a chemically distinct way for the addition to occur yielding the chiral product, (2R,3S)-isocitrate.

CONTRIBUTORS AND ATTRIBUTIONS

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