The acid-catalyzed dehydration of 1-butanol and 2-butanol and the base-induced dehydrobromination of 1-bromobutane and 2-bromobutane with strong base both lead to the formation of a mixture of butene isomers. The composition of this mixture varies, however, as a result of mechanistic differences in these two pathways.

A. Base-induced dehydrobromination of a secondary bromide:

Base-induced dehydrohalogenation of an alkyl halide is another alternative for synthesizing alkenes, and proceeds via an E2 mechanism. The use of strong and bulky base promotes the elimination reaction and disfavors the competing S_N2 reaction, which is disfavored when bulky reagents are used. The E2 reaction requires an anti-periplanar arrangement of the beta-H and leaving group (the beta-H and leaving group must be in the same plane and anti to each other). Because 2-bromobutane has two different types of beta-H’s, elimination on either side can lead to both internal and terminal alkenes (Scheme 1).

Scheme 1:

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1 A part of this procedure is adopted from an article published by H.M. Gilow in the Journal of Chemical Education, 1992, 69, A265.
Traditionally, E2 eliminations also follow Saytzeff’s rule. However, the use of a very bulky base can change the outcome of the reaction. When there are steric problems approaching one of the beta-hydrogens, the base will deprotonate the hydrogen that is least sterically hindered by adjacent alkyl groups. In the case of 2-bromobutane this is the hydrogen on the terminal methyl (CH$_3$) group resulting in the formation of the least substituted alkene. This elimination is called a Hofmann elimination.

**B. Base-induced dehydrobromination of a primary bromide:**

The base-induced dehydrohalogenation of 1-bromobutane is analogous to that of 2-bromobutane. Unlike 2-bromobutane, however, the halide resides on the terminal methyl group and therefore there is only one possible elimination (Scheme 2).


![Scheme 2:](image)

**C. Acid-catalyzed dehydration of a secondary alcohol:**

Dehydration of a secondary alcohol proceeds readily with the presence of strong acid such as sulfuric or phosphoric acid, and proceeds via an E1 mechanism (Scheme 3). In step 1, protonation of the hydroxyl group of the alcohol with the acid catalyst converts the poor leaving group -OH to a much better leaving group, H$_2$O. The loss of a water molecule from the oxonium ion intermediate results in a carbocation intermediate, which undergoes E1 elimination to form an alkene. If the elimination occurs with either one of the protons from the terminal methyl (CH$_3$) group, the resulting product is the terminal alkene – 1-butene. If the elimination occurs from the protons on the methylene (CH$_2$) group you get an internal alkene. Depending on which hydrogen is deprotonated you get either the cis- or trans-alkene. The least substituted alkene product is also known as the Hoffman product, and the Saytzeff products are the more-substituted, and therefore more stable alkenes. Of the two possible Saytzeff products, the trans-alkene is the most stable. Since the E1 reaction is under thermodynamic control, the relative stability of the resulting alkenes should determine the product distribution ratio. This is also known as Saytzeff’s rule.
According to LeChatelier's principle, removing a product from a chemical system at equilibrium shifts the equilibrium in the direction favoring the formation of the products. You will carry out the dehydration reaction in a reaction tube connected to a gas collector so that the product will continuously escape out of the reaction mixture as it is formed. Removal of the product will shift the equilibrium to the right and thus complete the reaction. The collected gaseous product will be analyzed by gas chromatography, which will show peaks with fair resolution. From the relative area of peaks, you can calculate the percentage composition of the product mixture.

D. Acid-catalyzed dehydration of a primary alcohol:

Dehydration of a primary alcohol proceeds analogously to that of a secondary one. The major difference is that instead of forming a secondary carbocation, the loss of a water molecule results in the formation of the much more unstable primary carbocation (Scheme 4). Elimination of that intermediate should result solely in the formation of the terminal alkene 1-butene. The high energy of the carbocation intermediate, however, might be so high in energy that no elimination reaction occurs.

E. A note about unexpected results:
Before running a reaction, chemists apply concepts from similar reactions to try and predict the results. Oftentimes, this works and the outcome is predicted correctly. Sometimes, this does not work and it is left to the scientist (you) to come up with a rationale for the results observed. Bear in mind that an unexpected outcome is not necessarily because the concepts you applied were wrong, but perhaps because something else is at work.

One or more reactions in this project might give unexpected results. Your job is to identify which reactions gave the expected results, which give unexpected results, and explain the unexpected results.