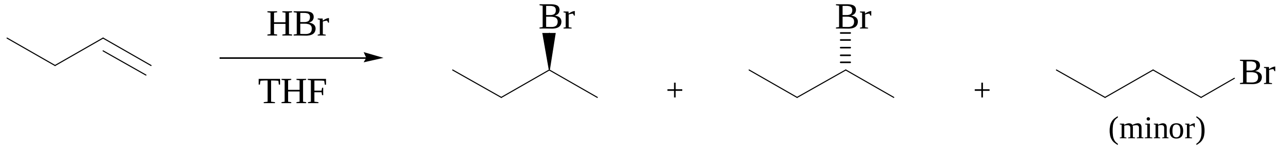
The Stereochemistry of Electrophilic Addition Reactions--Examples

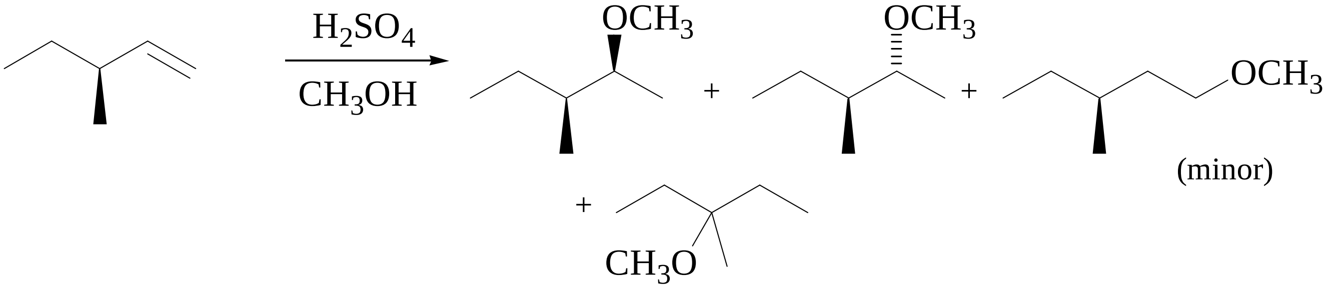
Shown below are six very specific reactions. In each case, ALL expected products are shown. The question is: What are these results telling us, or, alternatively, how could we have predicted them? See if the result in each case seems reasonable to you based on your knowledge of the mechanism of the reaction.

1.

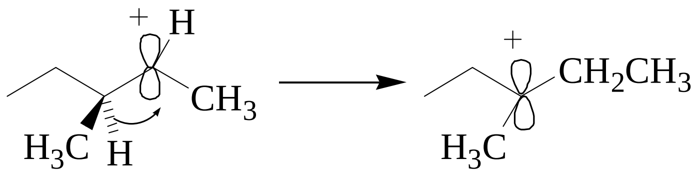


The reaction of HBr with 1-butene follows Markovnikov's Rule. There are three products expected, but the major product (a pair of enantiomers) arises from H$^+$ adding to the less substituted carbon in the first step; in the second step, Br$^-$ picks up the carbocation at the other (more substituted) carbon. The reaction of HBr with 1-butene is regioselective, because it gives more 2-bromobutane than 1-bromobutane, but it is not stereoselective, because the 2-bromobutane formed is a racemic mixture.

2.



The reaction of H_2SO_4 with (*S*)-3-methyl-1-pentene in methanol (the solvent) could produce four possible products. Two products, (2*S*,3*S*)-3-methyl-2-methoxypentane, and (2*R*,3*S*)-2-methoxy-3-methylpentane, are diastereomeric. They will not be produced in equal amounts, and there is no obvious way of predicting which will be formed more than the other. In this case there is also the possibility of rearrangement of the intermediate secondary carbocation (involving a 1,2-hydride shift). The product of rearrangement, 3-methoxy-3-methylpentane, is achiral. It has no asymmetric center and thus no enantiomer. The product of anti-Markovnikov addition, (*S*)-1-methoxy-3-methylpentane, is also possible, although we don't expect much of it.There is no reliable way to tell in this case what will be the major product of the reaction. One can guess that it will be a mess!



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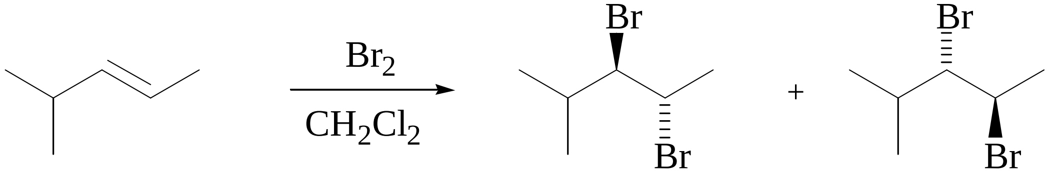
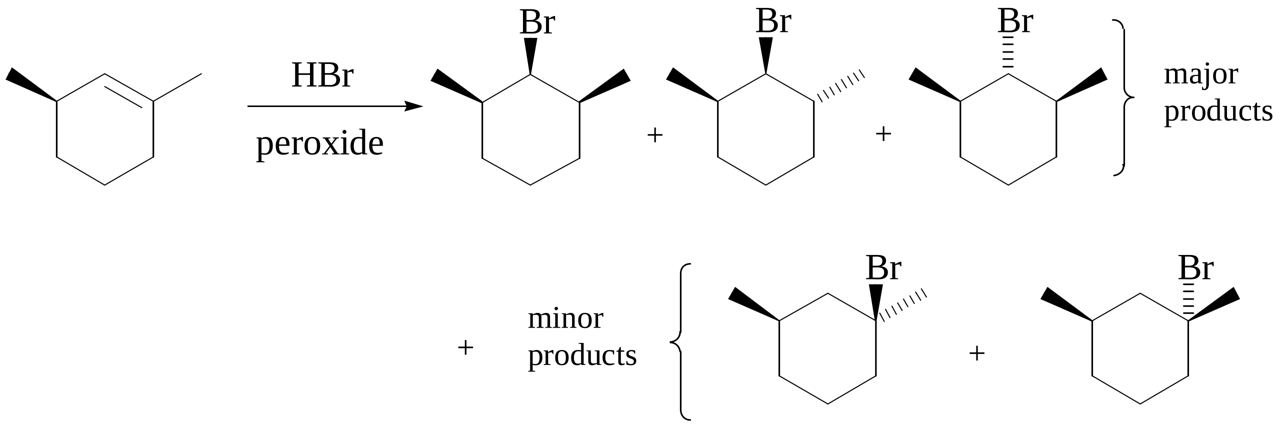


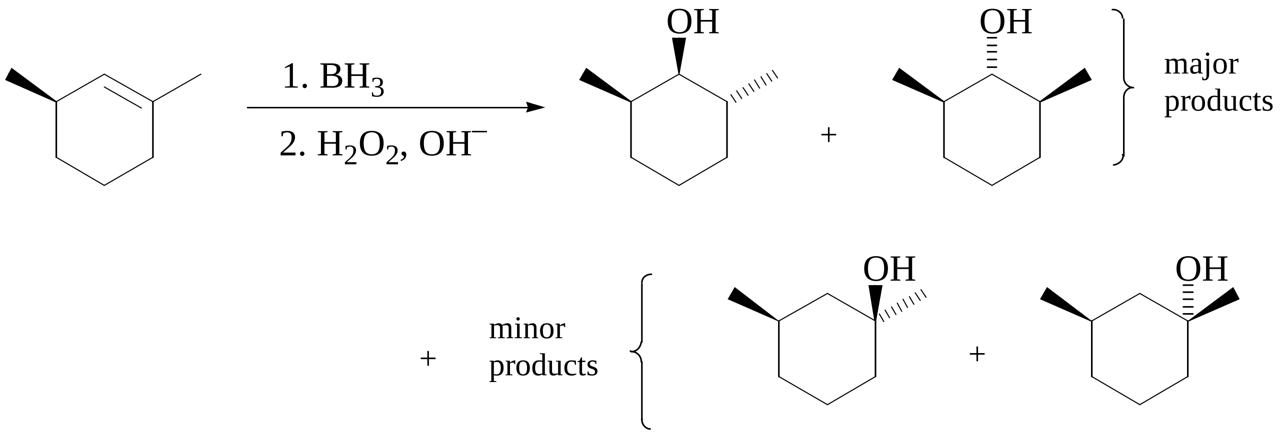
The reaction of bromine with *trans*-4-methyl-2-pentene leads to a racemic mixture of two enantiomers, (2*S*,3*R*)-2,3-dibromo-4-methylpentane and (2*R*,3*S*)-2,3-dibromo-4-methylpentane. The reaction is still considered to be stereoselective, because the product arises from exclusive *anti* addition of Br_2 across the double bond. (The two *syn*-addition stereoisomers aren't produced at all.) This *anti* addition is mandated by the mechanism, which involves a bromonium ion.

4.



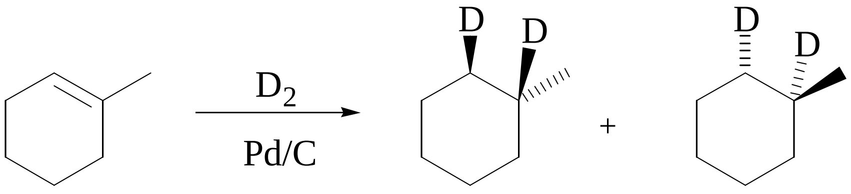
The radical addition of HBr to (*R*)-1,3-dimethylcyclohexene leads to a mixture of five products. Because of the presence of asymmetry in the reactant alkene, these products are not expected to be produced in equal amounts. We expect three isomers of 2-bromo-1,3-dimethylcyclohexane to be (collectively) the majority of the product. This mixture arises from the fact that the first addition of bromine radical can come from either face of the double bond, and then, in the second step, the abstraction of an H atom from a molecule of HBr can also come from either face of the sp^2 radical. (Interestingly, even though this sounds as though there would be four products, there IS no *fourth* isomer of 2-bromo-1,3-dimethylcyclohexane. How come?) Smaller (unequal) amounts of two diasteriomers of 1-bromo-1,3-dimethylcyclohexane (1*R*,3*R* and 1*S*,3*R*) are also expected. Another real mess!

5.



The *syn* addition of borane to (*R*)-1,3-dimethylcyclohexene and subsequent oxidation with basic hydrogen peroxide is expected to give four products. The major products are expected to be a pair of diasteriomers arising from the "anti-Markovnikov" addition of borane. Which of these two diastereomers will be produced in greater amount cannot be reliably predicted, although one might guess that the product of addition of borane from the opposite side of the ring as the CH_3 group might be more probable.

6.



The addition of D_2 to 1-methylcyclohexene is stereoselective because it produces only two of the four possible stereoisomers of 1,2-dideutero-1-methylcyclohexane (1*R*,2*R* and 1*S*,2*S*). The other two stereoisomers are not formed, because catalytic hydrogenation involves strictly *syn* addition to the double bond.