Addition of Bromine to Carbon–Carbon Double Bonds

The carbon–carbon double bond is one of the key functionalities encountered in organic chemistry. There are many reactions available in the toolbox of organic chemists to prepare alkenes, compounds with carbon–carbon double bonds. Because of the presence of π-electrons in such double bonds they are nucleophilic, and as a result are attacked by electrophilic reagents. One such reagent is molecular bromine, Br₂. The bromination of a carbon–carbon double bond is one of the oldest known reactions in organic chemistry. Even though the outcome of the reaction appears to be an addition of bromine across the double bond, the details of the mechanistic and stereochemical aspects are quite fascinating. Many of these studies are covered in standard undergraduate textbooks but quite frequently students find some of the concepts difficult to understand. An effort is made in this classroom item to discuss a few of these concepts, and to provide the results of some more recent investigations.

It has long been suspected that the addition of bromine to the C=C bond involves an intermediate, since the reaction carried out in the presence of a competing nucleophile gives (in addition to the dibromide) an addition product of bromine and the nucleophile. Two such examples are shown in Scheme 1.

Scheme 1
When two stereogenic (chiral) centers are present in a molecule, a total of four stereoisomers are possible in the form of two enantiomeric pairs. However, when the two centers are identical, there is only one enantiomeric pair (d/l pair) and a meso compound. The meso compound may be thought of as a molecule having two identical chiral centers of opposite configuration, with the result that it is optically inactive. A meso compound in the Fischer projection will have a plane of symmetry. In its more stable anti conformation, however, a meso compound will show a center of symmetry.

The stereochemical outcome of the bromination has also been studied in great detail. It was discovered that the overall addition of bromine is anti. In other words, the two bromine atoms appear to add from opposite faces of the double bond. This makes no difference if the alkene is ethylene, but if we take cis or trans 2-butenes as the substrates, anti addition to trans 2-butene would give the meso product (i.e., non-resolvable dibromide), whereas the cis isomer will produce the racemic mixture (i.e. resolvable dibromides).

These facts are consistent with the following mechanism, in which a bromonium ion is postulated as the intermediate.