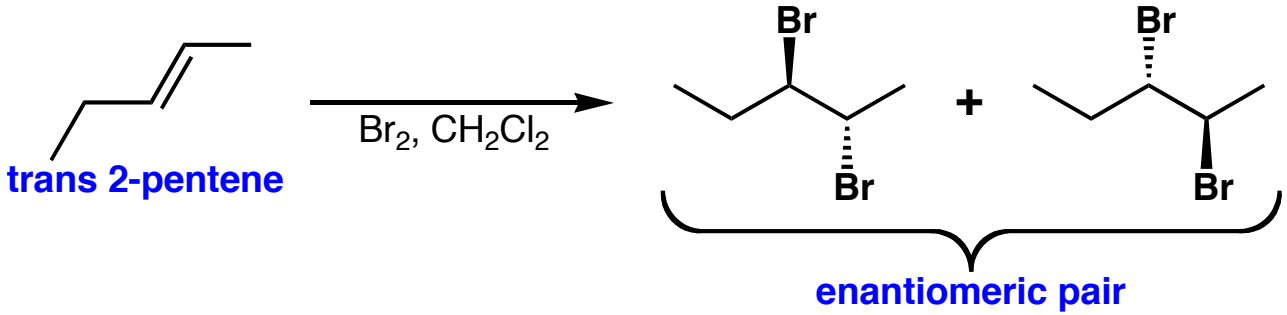
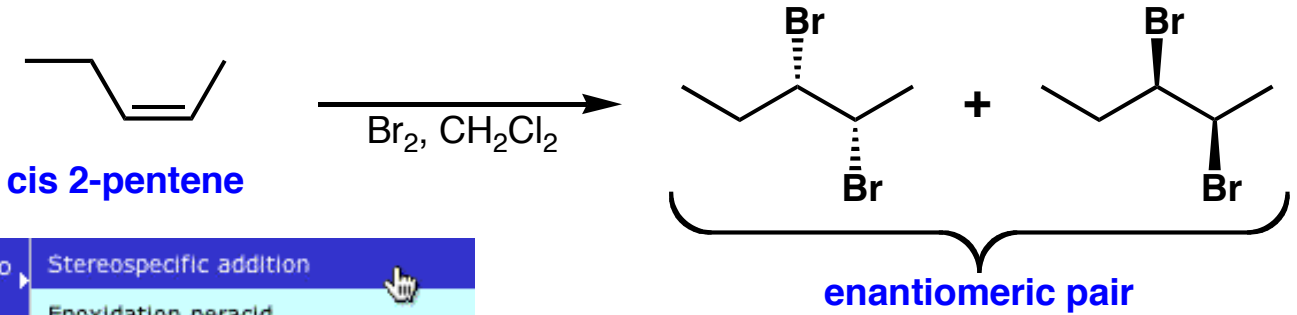
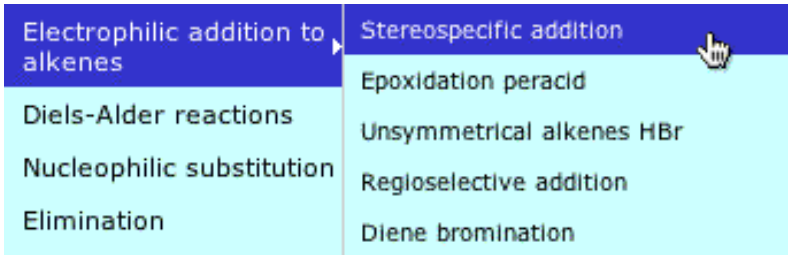
Halogens Add Stereospecifically to Alkenes

A mechanism that constrains the stereochemical outcome of a reaction is said to be stereospecific. Such a close relationship between mechanism and stereochemistry means that it is often possible to gain valuable insight into reaction mechanisms by studying their stereochemical features. This kind of a relationship is found for the addition of halogens to alkenes. In fact, the evidence that a bromonium ion was involved in alkene addition came from studies of the reaction stereochemistry. Consider the reactions of trans and cis 2-pentene shown below. The product has two stereocenters so up to four different stereoisomers are possible (there are no meso molecules in this case). Notice, however, that trans and cis substrates each give rise to unique subsets of the possible stereoisomers. The mechanism must account for these stereochemical observations.







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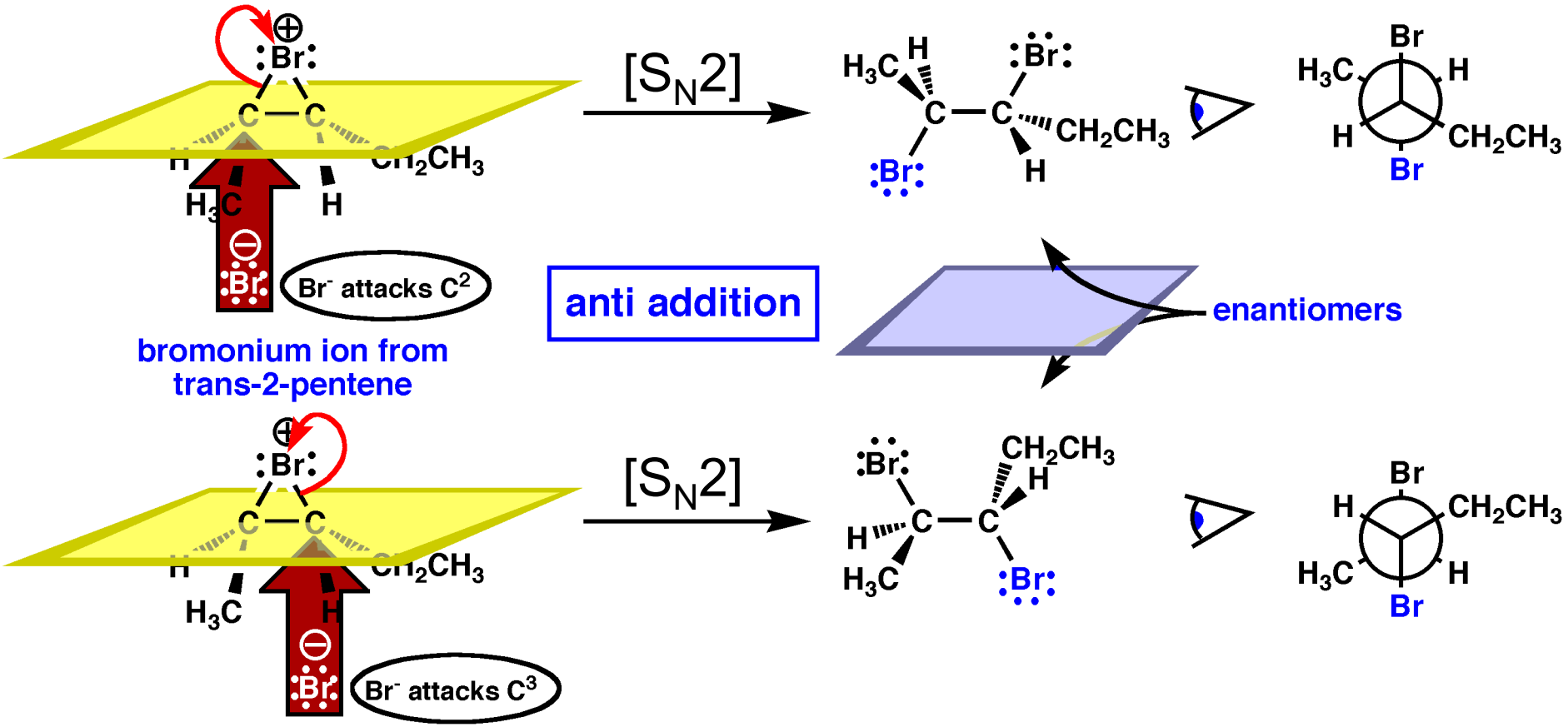
Rationalizing the Stereoisomers From Bromine Addition to Trans 2-Pentene

The addition of bromine to alkenes is a stereospecific reaction. In particular, the analysis below will show that this reaction is stereospecific for anti addition. The fact that the reaction follows anti addition provides important details of how the reaction mechanism must proceed. Trans 2-pentene gives rise to the bromonium ion shown below. The observed product is a mixture of enantiomers. These stereoisomers, being the only 2 of all the possible stereoisomeric products, can only come about if the Br^- nucleophile always attacks from the opposite side of Br^+, as expected for $n \rightarrow \sigma^*$ interaction of an [S_N2] step involving a bromonium ion intermediate. The different enantiomers arise from Br^- attack at the two different carbon atoms. The anti relationship of the bromine atoms can be seen in the Newman projection.



Rationalizing the Stereoisomers From Bromine Addition to Cis-2-Pentene

Bromine addition to cis-2-pentene produces a different set of enantiomers. However, the exact same mechanism discussed for the trans case also accounts for the stereoisomers produced in the cis case.