

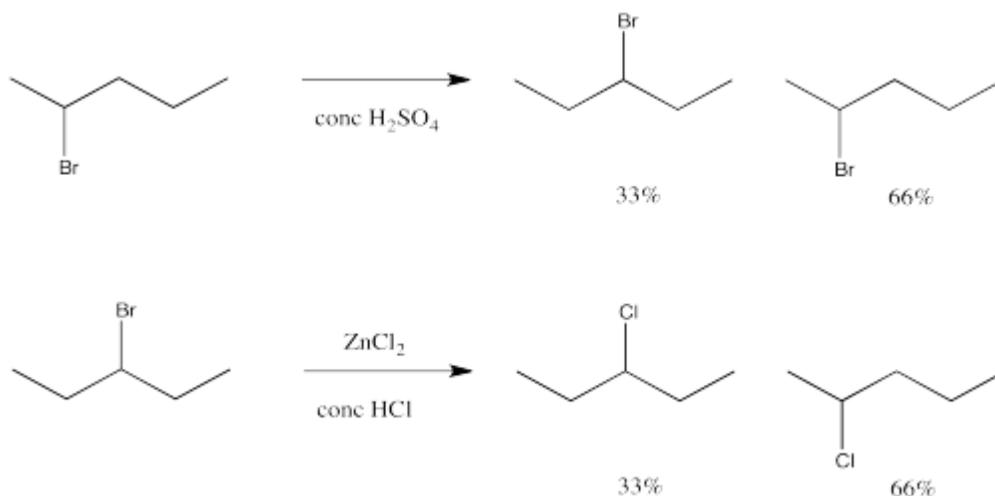
REGIOCHEMISTRY

Regiochemistry is the term for where changes take place in a reaction. It can be another indication of how the reaction occurred.

In aliphatic nucleophilic substitution, the answer seems pretty obvious: the reaction takes place at the electrophilic carbon, the one attached to the electronegative halogen. That's where the leaving group is. When the leaving group is replaced, that's where the nucleophile will be. But this isn't always true.

- In an S_N2 reaction, the nucleophile is always found on the carbon where the leaving group used to be.
- In an S_N1 reaction, the nucleophile is usually found on the carbon where the leaving group used to be. Sometimes it moves.

Under some circumstances, unexpected changes occur. The following two reactions are examples of such surprises. These reactions happen to take place via an S_N1 mechanism.



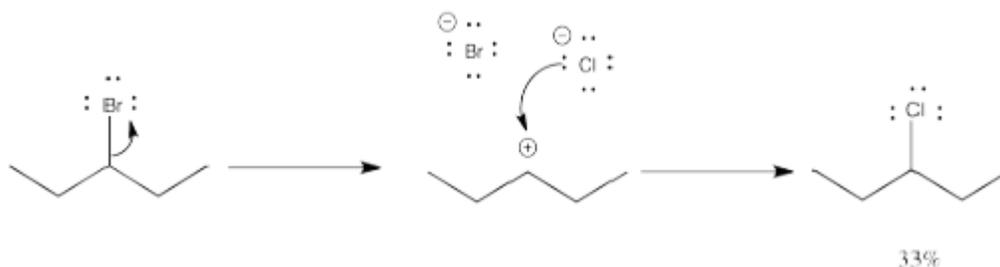
So, the regiochemistry of this reaction may be more complicated than we thought.

What is happening in these two reactions? In one of them, the bromine is just hopping from one place to another along the molecule. Some of the original compound remains, too, so there is a mixture. If you look carefully, though, the bromine has switched places with a hydrogen atom. It doesn't seem like that hydrogen atom could come off very easily.

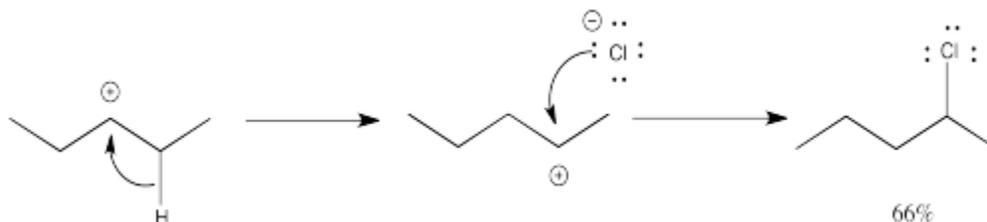
In the other reaction, something very similar is happening. Bromide and chloride both have lone pairs, so they can both be nucleophiles as well as leaving groups, and one can replace the other. There is lots of chloride around, so it beats any bromide to the electrophilic carbon. Once again, though, some of the chloride seems to end up in the wrong place.

This sort of behaviour is characteristic of carbocations. It is called a rearrangement, in which part of the molecule unexpectedly switches places.

Again, one of the products forms in a simple enough way.



The formation of the other product involves a "1,2-hydride shift". In this event, a hydrogen anion hops from one carbon to the next, leaving a cation where it used to be.



Source: <http://employees.csbsju.edu/cschaller/Reactivity/nusub/NSregiochem.htm>