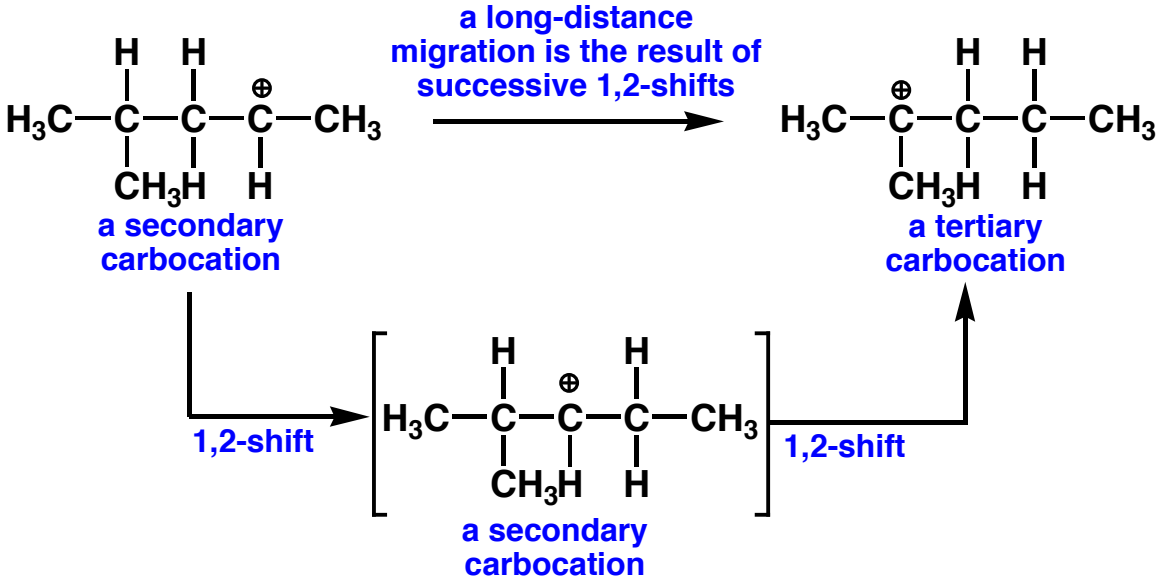
Carbocation Intermediates Undergo Rearrangement Reactions via 1,2-Shifts

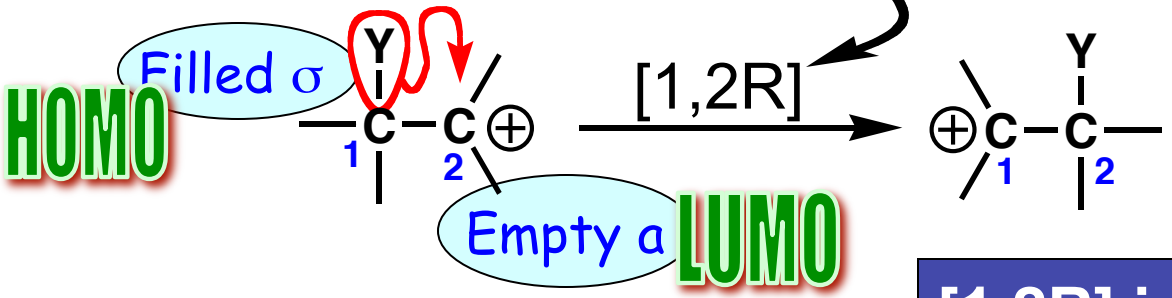
We have encountered carbocations in [S_N1] substitution and [E1] elimination. Any reaction that proceeds through carbocation intermediates may undergo a type of rearrangement reaction known as the 1,2-shift (also called 1,2-rearrangement). Recall from the seven classes of reactions that a rearrangement is a reaction with only a change in bonding connectivity. Typical groups undergoing 1,2-shifts are hydrogen (**hydride shift**), methyl (**methyl shift**), and C-C bonds in rings (**ring expansion**). These reactions are driven by formation of a more stable carbocation. The reactions may be reversible. It is possible for hydride and methyl migrations to take place over longer distances. However, when longer migrations do occur, they usually take place via a sequence of successive 1,2-shifts, not by a single-step, long-distance pathway.



Carbocation Rearrangements Require a New Elementary Step: The 1,2-Rearrangement [1,2R]

-Y is the group undergoing the 1,2-shift
-Y is typically -H, (hydride shift) or -CH_3

This symbol means a 1,2-rearrangement



[1,2R] involves σ-bond breaking, σ-bond making

[1,2R] involves a σ → *a* *π-type* interaction

The 1,2-shift involves migration of a sigma bond (its electrons and the attached atoms to that bond) from a carbon that is adjacent to the carbocation onto the carbocation. It is illustrated for the generic group labeled "Y". The 1,2-numbering reflects the fact that the migration takes place from atom labeled "1" to the adjacent atom labeled "2".

Curved Arrows Imply the Frontier Orbitals

Curved arrows indicate the HOMO-LUMO pair (Frontier Orbitals) involved in the elementary step. The tail of the arrow implies the filled orbital (HOMO) is an electron pair in a σ-bond. The head of the arrow points to the electron deficient carbon. An empty orbital on the carbocation is available to accommodate this electron pair implying that the LUMO is an atom-centered, empty orbital (*a*). The HOMO (σ-orbital) is beside (and nearly parallel to) the LUMO, *a*, allowing for a π-type interaction (σ-type overlap is not possible due to bonding constraints).

empty / filled	σ*	a	π*
σ	σ→σ*	σ→a	σ→π*
n	n→σ*	n→a	n→π*
π	π→σ*	π→a	π→π*