

Review on carbocation rearrangements:
1,2-hydride shifts or 1,2-alkyl shifts

In the past I have found student have a hard time knowing when to do a 1,2 shift, so here is a micro-review on carbocation rearrangements.

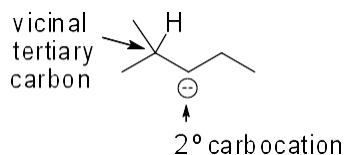
Carbocation rearrangements occur most frequently on secondary carbocations. Simple alkyl primary carbocations are too high in energy to form so you don't tend to see a primary carbocation. There are some exceptions to this general rule for primary carbocations. Certain structural conditions such as being benzylic or allylic, due to resonance, allows for the formation of primary carbocations. We have not learned about benzylic or allylic carbocations, but we will 😊. Tertiary carbocations do not need to rearrange as they are already the most stable.

If you generate a secondary carbocation as an intermediate in a reaction mechanism ***** always***** check to see if a rearrangement is possible. If a rearrangement is possible, you should rearrange the molecule in order to obtain the “major” product.

When are rearrangements possible?

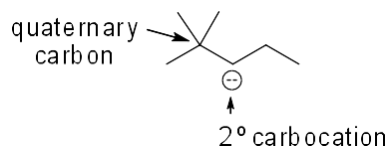
If a secondary carbocation is vicinal to a tertiary carbon bearing a hydrogen, a 1,2-hydride shift should occur.

Example of a secondary (2°) carbocation vicinal to a tertiary carbon



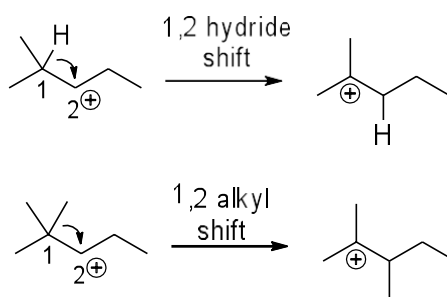
If a secondary carbocation is vicinal to a quaternary carbon, a 1,2-alkyl shift should occur. The general rule in alkyl shifts is: the smaller alkyl substituent tends to be the substituent that shifts. Therefore, the most common 1,2-alkyl shift is a 1,2-methyl shift.

Example of a secondary (2°) carbocation vicinal to a quaternary carbon



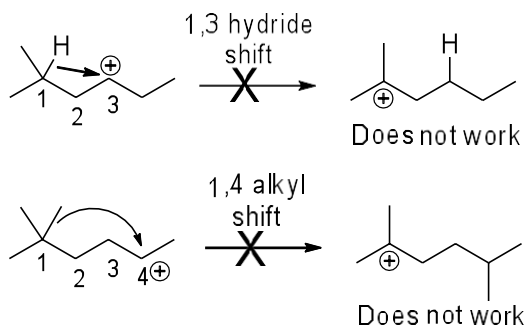
The mechanism of a 1,2-hydride shift and 1,2-alkyl shift.

The mechanism for a 1,2-hydride and a 1,2-alkyl shift are the same. The arrow (electron movement) starts at the bond of the substituent moving and points right at the carbocation. This shows that the atom/atoms in the substituent with the electrons moved to the carbocation. The shift (moving the electrons) results in a new carbocation where the substituent moved from.



When can you NOT do a shift?

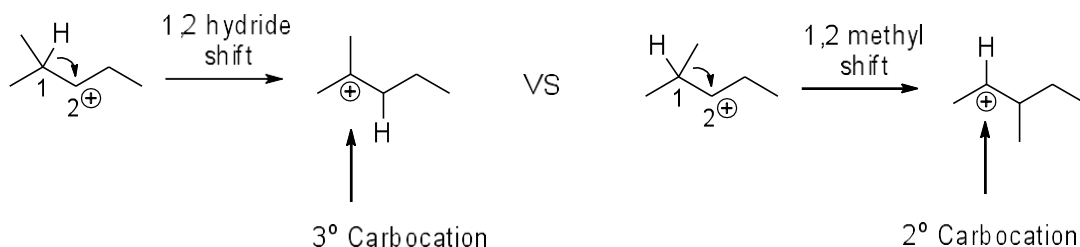
For the purpose of this course, you can not do a shift that is larger than 1,2. There are **NO** 1,3 or 1,4 ... shifts.



\$The million dollar questions\$
AKA the most common questions.

Q1:

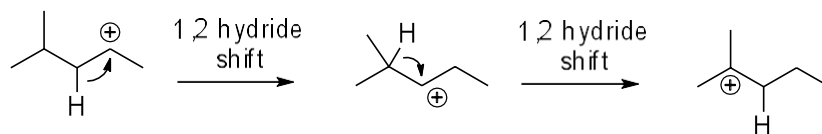
If you have a 2° carbocation next to a tertiary carbon that has a hydrogen why do you do a 1,2-hydride shift vs a 1,2-alkyl shift?



In this case if you had shifted the methyl you would have taken a 2° carbocation to a 2° carbocation. This is not favorable as there is no difference in energy between in the two carbocations. If you shift the hydride it goes from a 2° carbocation to a 3° carbocation.

Q2:

Why can I not do two consecutive 1,2-hydride shifts, which would ultimately result in a 3° carbocation?



Molecules do not “know” what their future holds; they just follow the lowest energy pathway. Since there is no energy difference of taking a 2° carbocation to another 2° carbocation, there is no reason for the initial shift to occur.

.....