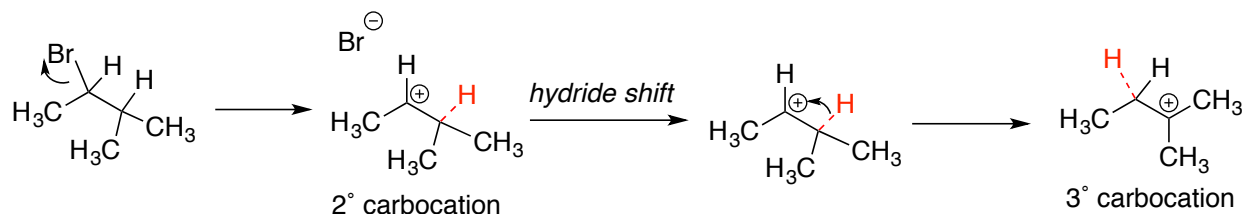


Carbocation Rearrangements

Because unimolecular reactions (S_N1 & E_1) proceed through a discrete carbocation intermediate, this intermediate has the opportunity to (rapidly!) undergo further changes before completion of the reaction. Specifically, the intermediate can rearrange from a less stable carbocation to a more stable carbocation.

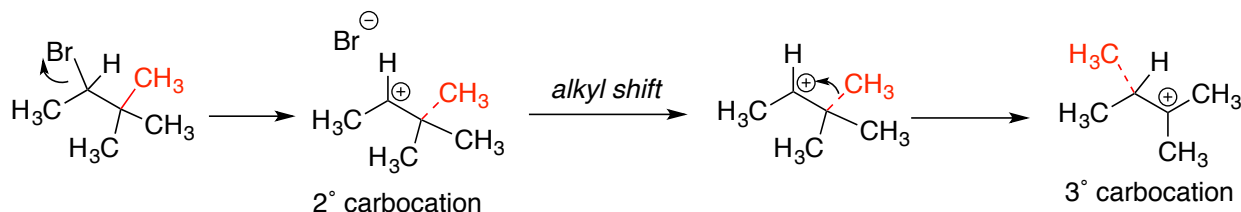
Hydride Shift



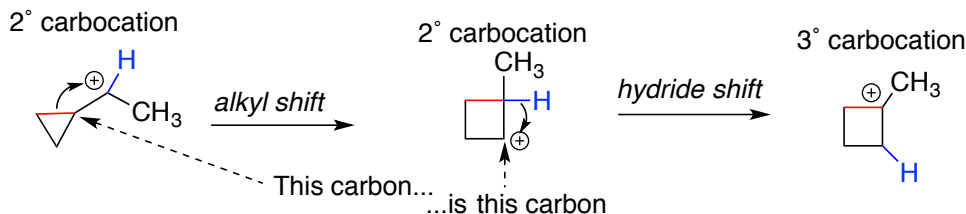
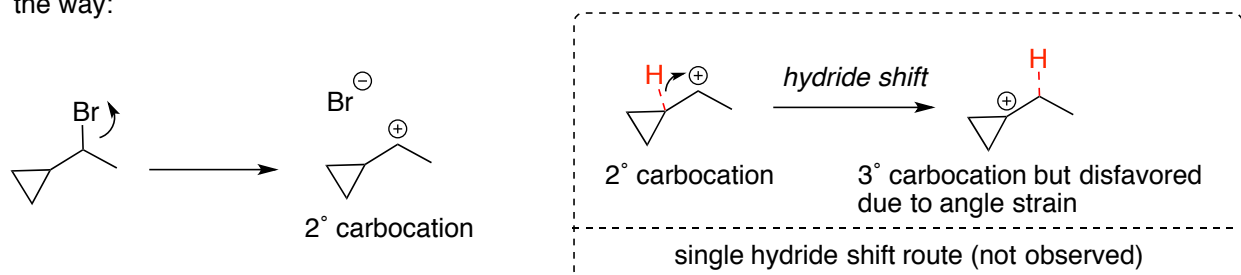
In this example, the departure of our Br leaving group leaves us with a 2° carbocation. However, migration of the hydride (the hydrogen atom along with both of the electrons from the dotted bond) to the 2° carbocation would leave us instead with a much more stable 3° carbocation.

Alkyl Shift

Alkyl groups may also shift to generate a more stable carbocation intermediate. As with hydride shifts, this is also rapid compared to intermolecular reactions.



Sequential shifts can happen as long as a more stable carbocation is generated at each individual step along the way:



The alkyl shift expands the ring, reducing ring strain, but still leaves a 2° carbocation. The subsequent hydride shift converts the new 2° carbocation into a much more stable 3° carbocation.

Sequential shifts (alkyl and hydride)