

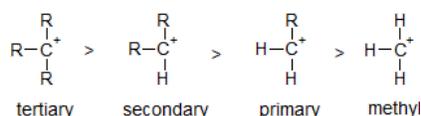
7.10: REARRANGEMENTS OF THE CARBOCATION AND S_N1 REACTIONS

Learning Objective

- predict carbocation rearrangements in 1st order reactions

Whenever reactants like alkyl halides form carbocations, the carbocations are subject to a phenomenon known as carbocation rearrangement. A carbocation is highly reactive and holds the positive charge on carbon with a sextet rather than an octet. There are two types of rearrangements: hydride shift and alkyl shift. Rearrangements occur to create more stable carbocations. Reviewing carbocation stability from chapter 5 is helpful in identifying carbocations that can undergo rearrangement.

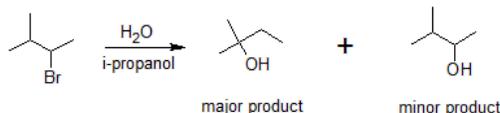
Relative Stability of Carbocations



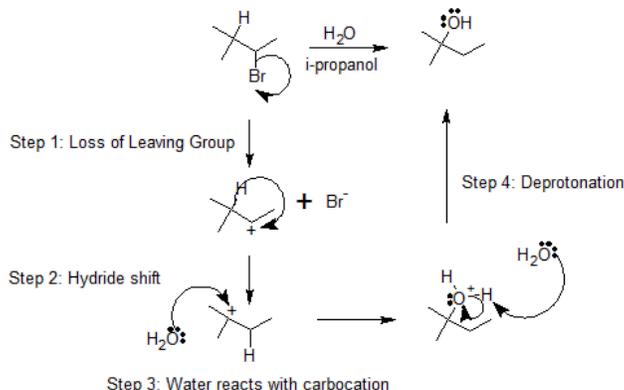
Once rearranged, the molecules can also undergo further unimolecular substitution (S_N1) or unimolecular elimination (E1). Nucleophilic reactions often produce two products, a major product and a minor product. The major product is typically the rearranged product that is more substituted (aka more stable). The minor product, in contrast, is typically the normal product that is less substituted (aka less stable). Similarly, we will see in subsequent sections of this chapter that for the unimolecular elimination reaction, a more substituted alkene can form through carbocation rearrangements ("stay tuned for coming attractions").

HYDRIDE SHIFT

The hydride shift can also be called the 1,2-Hydride Shift because rearrangements primarily occur between adjacent carbon atoms. The 1,2 are communicating that the carbons are vicinal (adjacent). These numbers have nothing to do with the nomenclature of the reactant. We can see the phenomenon of hydride shift in solvolysis (S_N1) reactions like the example below.



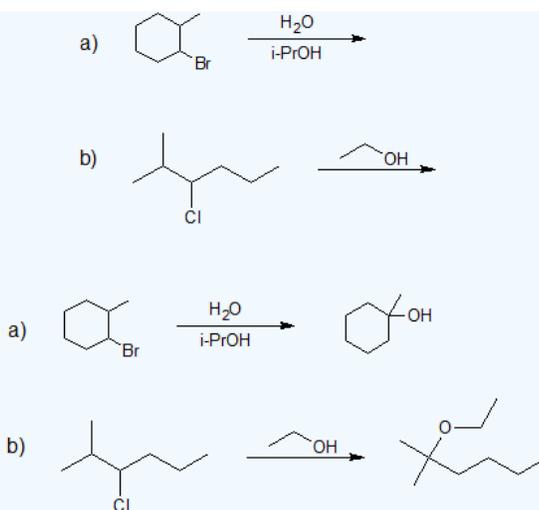
As shown in the following mechanism, the polarized carbon-chlorine bond is heterolytically broken to produce a chloride ion and carbocation. The secondary carbocation undergoes a 1,2 hydride shift to produce the more stable tertiary carbocation. The oxygen of a water molecule acts as the nucleophile and reacts with the carbocation to form a protonated alcohol. The intermediate is deprotonated to form the final product, an alcohol. The mechanism for hydride shift occurs in *multiple steps* that includes various intermediates and transition states.



Exercise

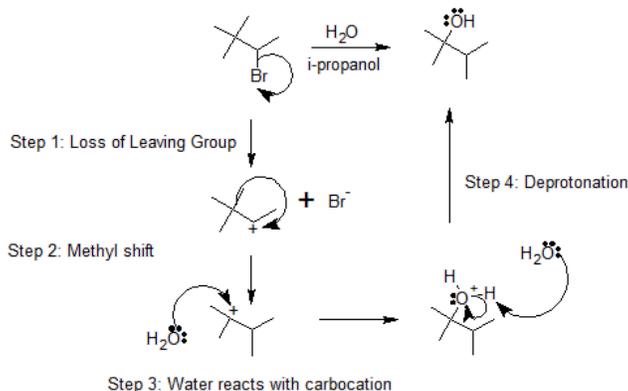
- Draw the bond-line structure for the major solvolysis product of each reaction.

Answer



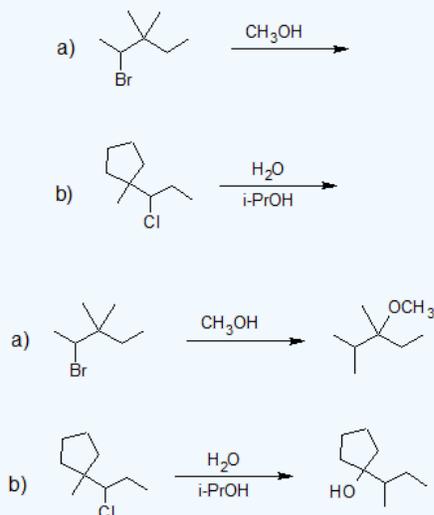
ALKYL SHIFT

Not all carbocations have suitable hydrogen atoms (either secondary or tertiary) that are on adjacent carbon atoms available for rearrangement. In this case, the reaction can undergo a different mode of rearrangement known as **alkyl shift** (or alkyl group migration). Alkyl Shift acts very similarly to that of hydride shift. Instead of the proton (H) that shifts with the nucleophile, we see an alkyl group that shifts with the nucleophile instead. The shifting group carries its electron pair with it to furnish a bond to the neighboring or adjacent carbocation. The shifted alkyl group and the positive charge of the carbocation switch positions on the molecule.



Exercise

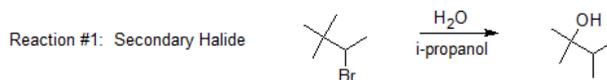
2. Draw the bond-line structure for the major solvolysis product of each reaction.



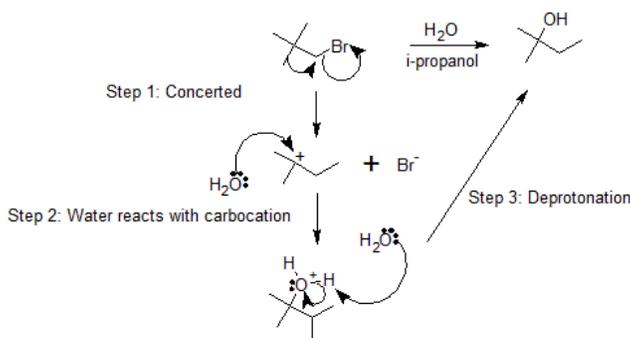
Answer

Alkyl Halide Classification and Carbocation Rearrangements

Reactions of tertiary carbocations react much faster than that of secondary carbocations and will form the major product almost exclusively. Alkyl shifts from a secondary carbocation to tertiary carbocation in S_N1 reactions occur by independent steps. When the alkyl halide is primary, then slight variations and differences between the two reaction mechanisms. In reaction #1, we see that we have a secondary substrate. This undergoes alkyl shift because it does not have a suitable hydrogen on the adjacent carbon. Once again, the reaction is similar to hydride shift. The only difference is that we shift an alkyl group rather than shift a proton, while still undergoing various intermediate steps to furnish its final product.

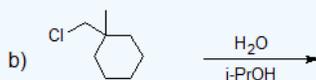


With reaction #2, on the other hand, we can say that it undergoes a *concerted* mechanism. In short, this means that everything happens in one step. This is because primary carbocations *cannot* be an intermediate and they are relatively difficult processes since they require higher temperatures and longer reaction times. After protonating the alcohol substrate to form the alkyloxonium ion, the water must leave *at the same time* as the alkyl group shifts from the adjacent carbon to skip the formation of the unstable primary carbocation.

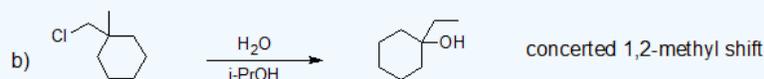
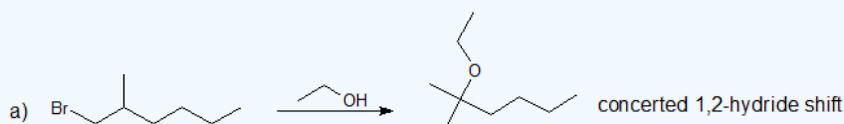


Exercise

3. Draw the bond-line structure for the major solvolysis product of each reaction.



Answer



1,3-HYDRIDE AND GREATER SHIFTS

Typically, hydride shifts can occur at low temperatures. However, by heating the solution of a cation, it can easily and readily speed the process of rearrangement. One way to account for a slight barrier is to propose a 1,3-hydride shift interchanging the functionality of two different kinds of methyls. Another possibility is 1,2 hydride shift in which you could yield a secondary carbocation intermediate. Then, a further 1,2 hydride shift would give the more stable rearranged tertiary cation.

More distant hydride shifts have been observed, such as 1,4 and 1,5 hydride shifts, but these arrangements are too fast to undergo secondary cation intermediates.

ANALOGY

Carbocation rearrangements happen very readily and often occur in many organic chemistry reactions. Yet, we typically neglect this step. Dr. Sarah Lievens, a Chemistry professor at the University of California, Davis once said carbocation rearrangements can be observed with various analogies to help her students remember this phenomenon. For hydride shifts: "The new friend (nucleophile) just joined a group (the organic molecule). Because he is new, he only made two new friends. However, the popular kid (the hydrogen) gladly gave up his friends to the new friend so that he could have even more friends. Therefore, everyone won't be as lonely and we can all be friends." This analogy works for alkyl shifts in conjunction with hydride shift as well.

REFERENCES

1. Vogel, Pierre. Carbocation Chemistry. Amsterdam: Elsevier Science Publishers B.V., 1985.
2. Olah, George A. and Prakash, G.K. Surya. Carbocation Chemistry. New Jersey: John Wiley & Sons, Inc., 2004.
3. Vollhardt, K. Peter C. and Schore, Neil E. Organic Chemistry: Structure and Function. New York: Bleyer, Brennan, 2007.

OUTSIDE LINKS

- [en.Wikipedia.org/wiki/Carbocation_rearrangement](https://en.wikipedia.org/wiki/Carbocation_rearrangement)
- [Watch a short presentation on the carbocation rearrangement phenomenon](#)

CONTRIBUTORS AND ATTRIBUTIONS

- Jeffrey Ma

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