

REARRANGEMENT OF CARBOCATIONS DERIVED FROM ALCOHOLS

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Introduction:

In the intricate realm of organic chemistry, the rearrangement of carbocations stands as a fascinating and pivotal phenomenon, offering profound insights into the dynamic nature of molecular structures. Among the myriad sources from which carbocations can be derived, alcohols emerge as a particularly intriguing starting point. This article delves into the captivating world of rearrangements involving carbocations originating from alcohols, exploring the underlying principles, mechanisms, and the consequential impact on reaction pathways.

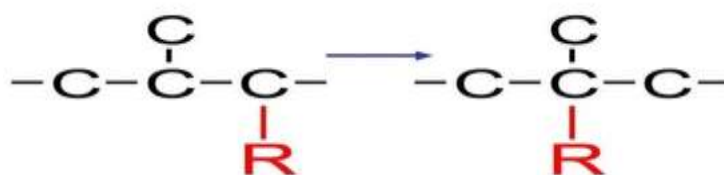
Carbocations, or positively charged carbon species, are transient intermediates that play a pivotal role in various organic reactions. The rearrangement of these species adds an additional layer of complexity, providing chemists with both challenges and opportunities for understanding and manipulating chemical transformations. When carbocations are derived from alcohols, the intricacies of their rearrangement processes become even more intriguing due to the unique structural features and electronic characteristics inherent to alcohol-derived carbocations.

This exploration aims to unravel the factors influencing the rearrangement of carbocations derived from alcohols, shedding light on the driving forces behind these transformations. As we journey through the molecular landscape, we will delve into key theoretical frameworks, experimental observations, and real-world applications, ultimately enhancing our comprehension of this captivating facet of organic chemistry.

Key words: carbocation, rearrangement, alcohol, major product, hydrogen chloride, hydride shift, alkyl shift, unimolecular elimination, unimolecular substitution.

Whenever alcohols are subject to transformation into various carbocations, the carbocations are subject to a phenomenon known as carbocation rearrangement. A carbocation, in brief, holds the positive charge in the molecule that is attached to three

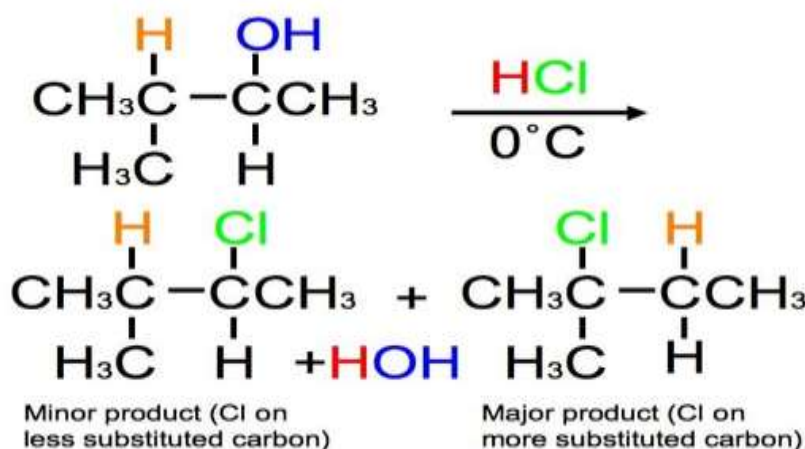
other groups and bears a sextet rather than an octet. However, we do see carbocation rearrangements in reactions that do not contain alcohol as well. Those, on the other hand, require more difficult explanations than the two listed below. There are two types of rearrangements: hydride shift and alkyl shift. These rearrangements usually occur in many types of carbocations. Once rearranged, the molecules can also undergo further unimolecular substitution (S_N1) or unimolecular elimination (E_1). Though, most of the time we see either a simple or complex mixture of products. We can expect two products before undergoing carbocation rearrangement, but once undergoing this phenomenon, we see the major product.



Hydride Shift:

Whenever a nucleophile attacks some molecules, we typically see two products. However, in most cases, we normally see both 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).

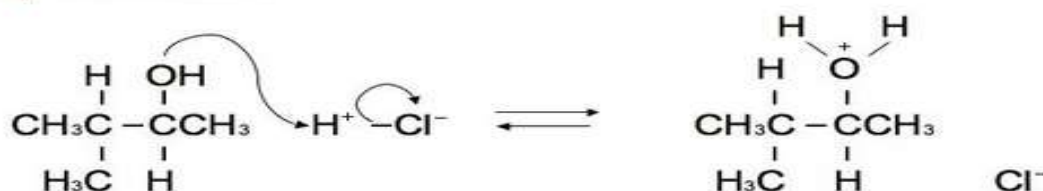
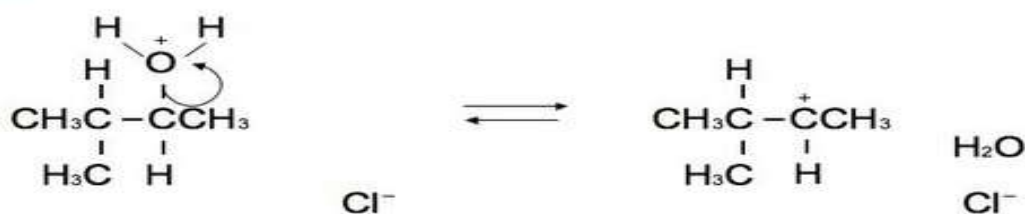
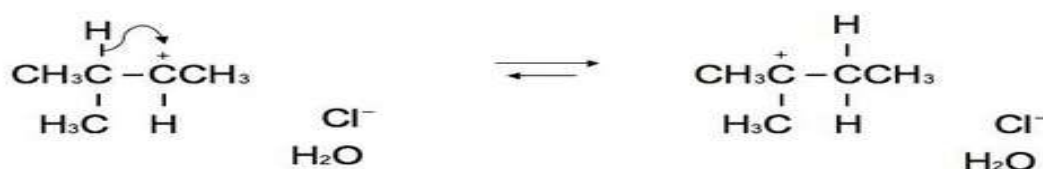
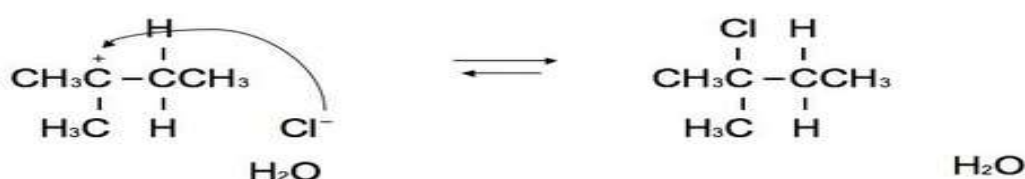
The reaction: We see that the formed carbocations can undergo rearrangements called hydride shift. This means that the two electron hydrogen from the unimolecular substitution moves over to the neighboring carbon. We see the phenomenon of hydride shift typically with the reaction of an alcohol and hydrogen halides, which include HBr, HCl, and HI. HF is typically not used because of its instability and its fast reactivity rate. Below is an example of a reaction between an alcohol and hydrogen chloride:



GREEN (Cl) = nucleophile; BLUE (OH) = leaving group;

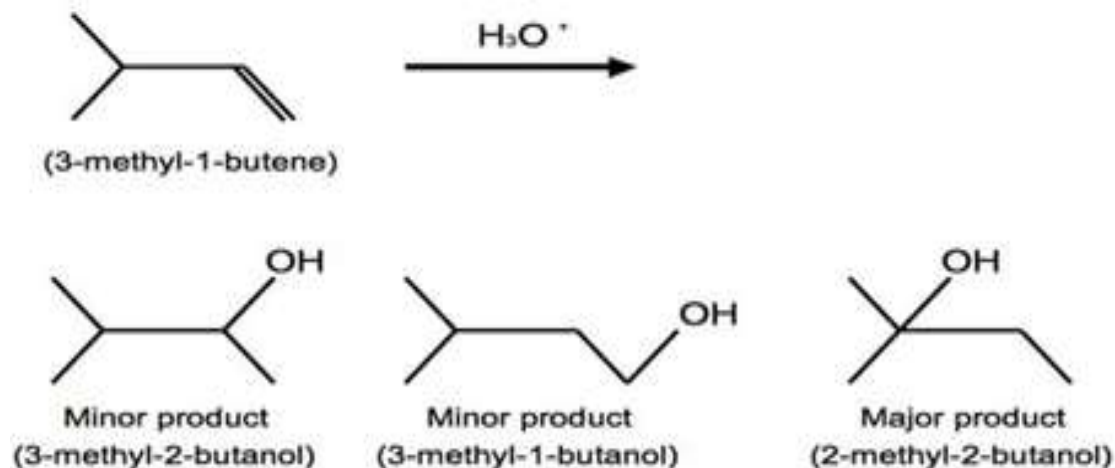
ORANGE (H) = hydride shift proton; RED(H) = remaining proton

The alcohol portion (-OH) has been substituted with the nucleophilic Cl atom. However, it is not a direct substitution of the OH atom as seen in S_N2 reactions. In this S_N1 reaction, we see that the leaving group, -OH, forms a carbocation on Carbon №3 after receiving a proton from the nucleophile to produce an alkyloxonium ion. Before the Cl atom attacks, the hydrogen atom attached to the Carbon atom directly adjacent to the original Carbon (preferably the more stable Carbon), Carbon №2, can undergo hydride shift. The hydrogen and the carbocation formally switch positions. The Cl atom can now attack the carbocation, in which it forms the more stable structure because of hyperconjugation. The carbocation, in this case, is most stable because it attaches to the tertiary carbon (being attached to 3 different carbons). However, we can still see small amounts of the minor, unstable product. The mechanism for hydride shift occurs in multiple steps that includes various intermediates and transition states. Below is the mechanism for the given reaction above:

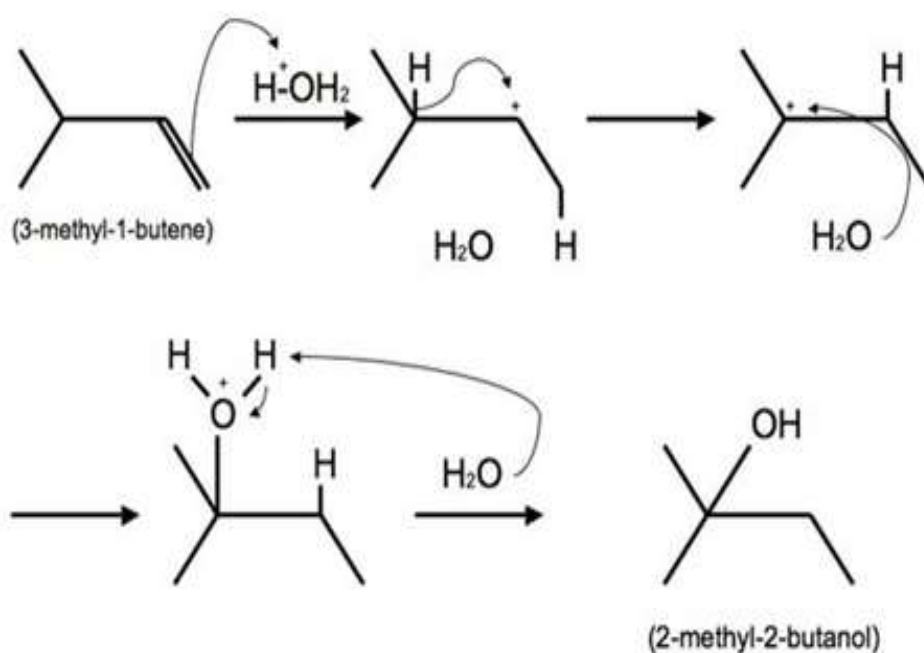
Step 1: Protonation**Step 2: Loss of H₂O****Step 3: Hydride Shift****Step 4: Chlorine Attacks**

Hydration of Alkenes: Hydride Shift

In a more complex case, when alkenes undergo hydration, we also observe hydride shift. Below is the reaction of 3-methyl-1-butene with H_3O^+ that furnishes to make 2-methyl-2-butanol:



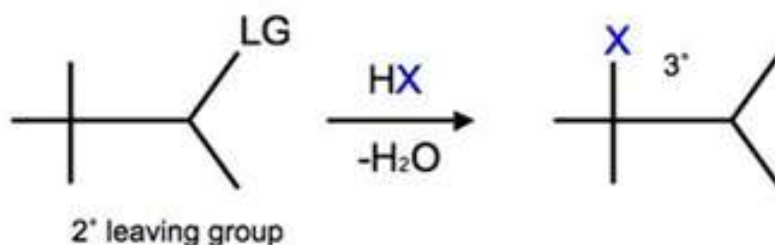
Once again, we see multiple products. In this case, however, we see two minor products and one major product. We observe the major product because the $-\text{OH}$ substituent is attached to the more substituted carbon. When the reactant undergoes hydration, the proton attaches to carbon №2. The carbocation is therefore on carbon №2. Hydride shift now occurs when the hydrogen on the adjacent carbon formally switch places with the carbocation. The carbocation is now ready to be attacked by H_2O to furnish an alkyloxonium ion because of stability and hyperconjugation. The final step can be observed by another water molecule attacking the proton on the alkyloxonium ion to furnish an alcohol. We see this mechanism below:



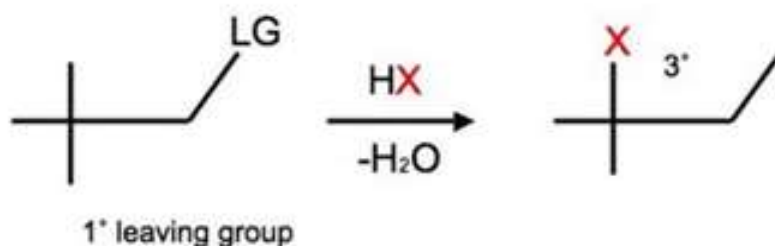
Alkyl Shift:

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. Reactions of tertiary carbocations react much faster than that of secondary carbocations. We see alkyl shift from a secondary carbocation to tertiary carbocation in S_{N1} reactions:

Reaction #1: Secondary Substrate



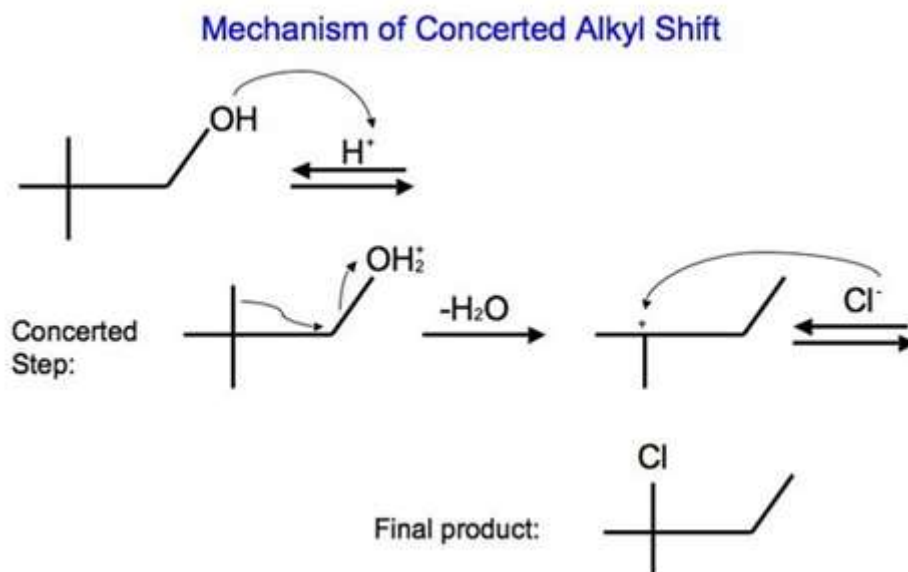
Reaction #2: Primary Substrate



We observe slight variations and differences between the two reactions. 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.



Conclusion:

In concluding our exploration of the rearrangement of carbocations derived from alcohols, we find ourselves at the intersection of fundamental understanding and practical application in organic chemistry. The journey through this intricate domain has unveiled the nuanced factors influencing the rearrangement processes and highlighted the significance of alcohol-derived carbocations in shaping reaction outcomes.

As we reflect on the mechanisms and driving forces behind these rearrangements, it becomes evident that the interplay of structural factors, electronic effects, and environmental conditions dictates the intricate dance of atoms within these transient intermediates. The dynamic nature of alcohol-derived carbocations not only enriches our comprehension of reaction mechanisms but also inspires the design of strategic synthetic pathways.

The implications of this exploration extend far beyond the laboratory bench. The knowledge gained from studying the rearrangement of carbocations derived from alcohols opens avenues for innovation in diverse fields, from drug discovery to materials science. Harnessing this understanding can empower chemists to fine-tune reaction conditions, optimize selectivity, and unlock new possibilities in the synthesis of complex organic molecules.

Furthermore, the insights gained contribute to the broader narrative of sustainable and efficient chemical synthesis. By deciphering the intricacies of carbocation rearrangements, researchers are better equipped to develop greener methodologies, minimizing waste and maximizing resource efficiency.

In essence, our journey through the rearrangement of carbocations derived from alcohols underscores the dynamic nature of organic chemistry, where molecular rearrangements serve as a testament to the profound interconnectedness of chemical species. As we look ahead, armed with newfound knowledge, we anticipate that continued exploration in this field will fuel discoveries that shape the landscape of organic synthesis, pushing the boundaries of what is chemically conceivable.

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