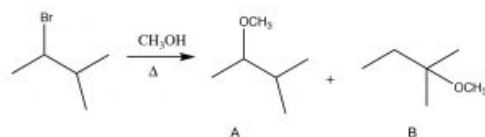


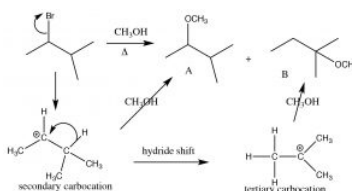
4.3: Rearrangements- A Consequence of Generating Unstable Carbocations

Reactions that generate carbocations can undergo reaction pathways besides substitution.

Consider this reaction:

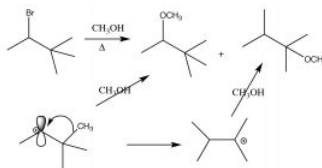


The substrate is a secondary alkyl halide, and since the solvent is methanol, a polar protic solvent, and with a weak nucleophile, we would expect an $\text{S}_{\text{N}}1$ reaction to occur, via a carbocation at the secondary carbon. The first product (A) is exactly that, but how did the second product (B) form? To understand this, let us look at the mechanism of the reaction. The first step is the ionization of Br⁻ to leave behind the secondary carbocation (which produces product A). Product B must have been formed by nucleophilic attack of the O in methanol onto a different carbocation. The precursor to B is a tertiary carbocation, which is more stable than the secondary, and it is formed by what is known as a hydride shift in which the hydrogen shifts with its pair of electrons.



Formation of carbocations is often accompanied by a skeletal rearrangement: Here a 1,2 hydride shift occurs

This rearrangement produces a more stable intermediate that then undergoes reaction; it can also involve the shift of an alkyl group with its electrons from one carbon to the next.



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