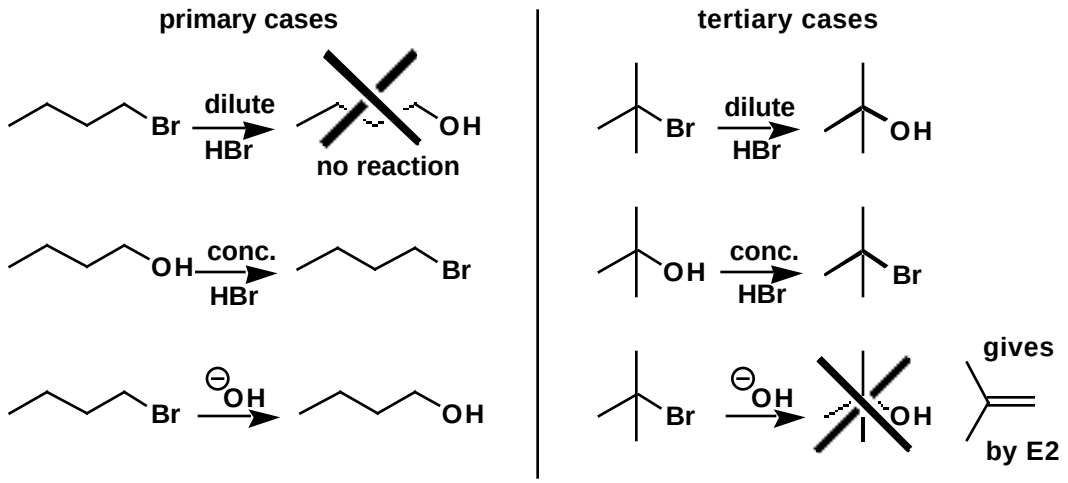
Text Related to Segment 14.05 ©2002 Claude E. Wintner

Let us conclude by reviewing the contrasts in the outcomes of S_N reactions for primary and tertiary cases. The relatively mildly acidic conditions of dilute HBr are S_N1 conditions that can lead to alcohols (first line of the figure). The reaction is blocked for primary halides, because primary carbocations lie at too high an energy, so that they are not available as viable intermediates. To repeat: any substitution reaction observed at a primary center will not take place through a unimolecular mechanism. On the other hand, for tertiary halides in dilute HBr the carbocation can form.



summary of S_N reactions

Moving to the next line of the figure, the strongly acidic conditions of concentrated HBr with alcohols support the S_N2 mechanism for primary cases, where the alcohol can be protonated to yield an oxonium ion in a pre-equilibrium step, after which bromide ion displaces water. (Bromide ion does *not* displace hydroxide ion, nor can hydroxide ion be invoked in acid solution!) For tertiary alcohols the same pre-equilibrium with an oxonium ion is established in concentrated HBr; however, an S_N1 reaction then ensues, the outcome again being the alkyl bromide, formed as a result of the success of the excess bromide ion in competition

with water for the tertiary carbocation. Finally (last line), basic conditions, such as hydroxide ion, are S_N2 conditions. Reaction is blocked in tertiary cases because of the steric effect; any substitution at a tertiary center will not be through a bimolecular mechanism, and any second order reaction observed for a tertiary center under basic conditions will not be a substitution reaction, but rather an elimination taking place via the competing E2 mechanism. As might be expected, secondary cases present intermediate properties and can be difficult to predict: secondary cations are less stable than tertiary ones, but on the other hand often are not hopelessly unstable, while coaxial S_N2 attack from the rear in secondary situations generally is hindered, but often is not impossibly blocked.

©2002 Claude E. Wintner