The formation of carbocations is sometimes accompanied by a structural rearrangement. Such rearrangements take place by a shift of a neighboring alkyl group or hydrogen, and are favored when the rearranged carbocation is more stable than the initial cation. The addition of HCl to 3,3-dimethyl-1-butene, for example, leads to an unexpected product, 2-chloro-2,3-dimethylbutane, in somewhat greater yield than 3-chloro-2,2-dimethylbutane, the expected Markovnikov product. This surprising result may be explained by a carbocation rearrangement of the initially formed 2º-carbocation to a 3º-carbocation by a 1,2-shift of a methyl group.

Another factor that may induce rearrangement of carbocation intermediates is strain. The addition of HCl to α-pinene, the major hydrocarbon component of turpentine, gives the rearranged product, bornyl chloride, in high yield. As shown in the following equation, this rearrangement converts a 3º-carbocation to a 2º-carbocation, a transformation that is normally unfavorable. However, the rearrangement also expands a strained four-membered ring to a much less-strained five-membered ring, and this relief of strain provides a driving force for the rearrangement. The atom numbers (colored red) for the pinene structure are retained throughout the rearrangement to help orient the viewer. The green numbers in the final product represent the proper numbering of this bicyclic ring system.

The propensity for structural rearrangement shown by certain molecular constitutions, as illustrated above, serves as a useful probe for the intermediacy of carbocations in a reaction. We shall use this test later.

**Contributors**