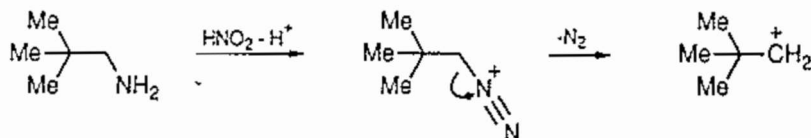
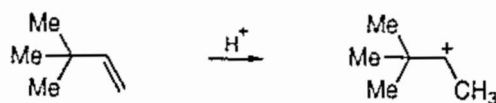


(3) From an amine, by treatment with nitrous acid: reaction occurs *via* the aliphatic diazonium ion from which molecular nitrogen is rapidly lost,



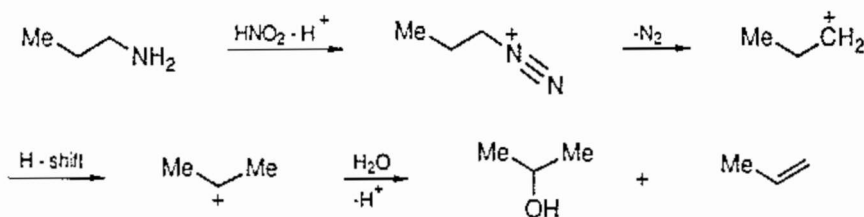
(4) From an alkene by protonation, e.g.



2. *Hydrogen can also migrate in these systems.* For example, reactions which occur through the isobutyl cation yield mainly products derived from the t-butyl cation:



A typical example of a hydride shift occurs in the reaction of a primary aliphatic amine with nitrous acid, e.g.



3. *Aryl groups have a far greater migratory aptitude than alkyl groups or hydrogen.* For example, the chloride below undergoes solvolysis with rearrangement many thousands of times faster than neopentyl chloride in the same conditions. This is ascribed to the fact that, whereas the rate-determining step in the reaction of neopentyl chloride is the formation of the high-energy primary carbocation, that in the reaction of the phenyl-substituted chloride is the formation of a lower-energy bridged phenonium ion:

