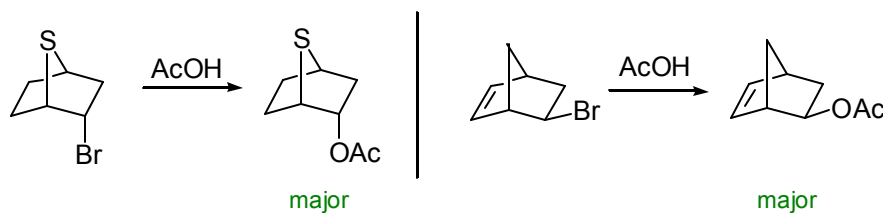
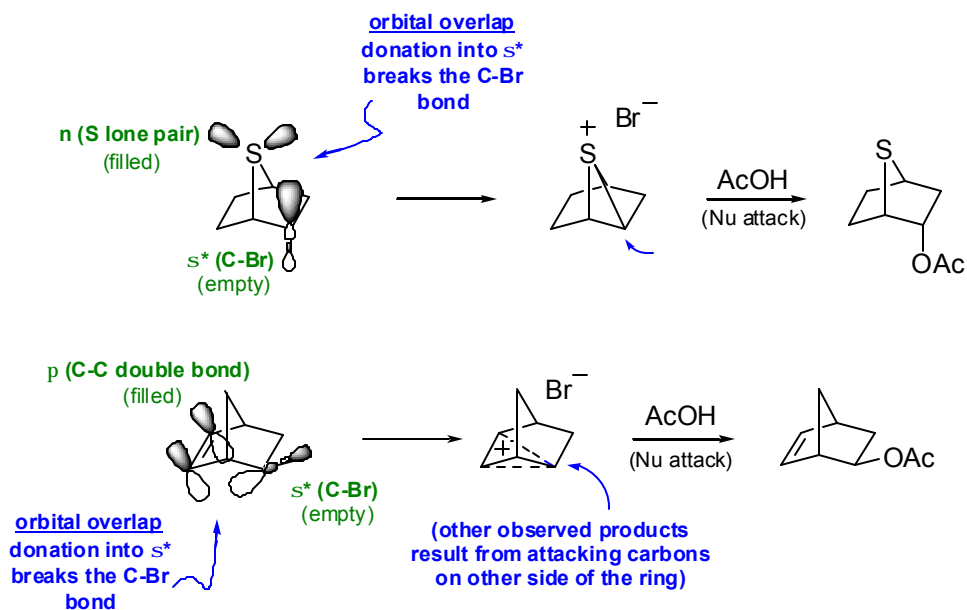


Problem 2. Note that the following substitution reactions proceed with retention of configuration despite being conducted under standard S_N2 conditions. Provide an explanation for this observation, being sure to touch on molecular orbital theory.



Solution



- In both cases, the molecules have geometries such that relatively high-energy filled orbitals (good electron donors) can interact with relatively low-energy unfilled orbitals (good electron acceptors). Because Br^- is a good leaving group, these can proceed as intramolecular “ S_N2 -like” reactions to generate carbocation intermediates.
- These carbocations are subsequently attacked by the nucleophilic solvent in solvolysis reactions. Double inversion of stereochemistry from two S_N2 -like reactions results in the observed retention of configuration.
- Side note: These reactions have additional products that have been excluded here for simplicity

Key Lessons

- Be on the look out for intramolecular orbital interactions between filled orbitals (typically π or n) and unfilled orbitals (typically antibonding orbitals, especially σ^*). These interactions can lead to increased stability or intramolecular reactions (as shown above).
- Retention of stereochemistry can be caused by two stereospecific inversions.