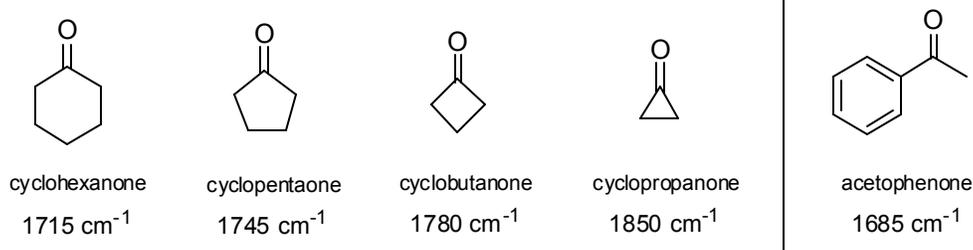


Section Solution Set

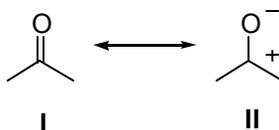
Orbitals and Bonding

Problem 1 (data provided in Loudon, 4 ed., p. 845). Provide an explanation for the following observed trend for the IR absorptions corresponding to C=O stretching in these cyclic ketones.



Solution

- Recall from Chem 20 that the wavenumber of absorption is directly proportional to the energy associated with the mode of oscillation (here a C=O stretch). As the “stiffness” of the bond increases, the energy associated with bond stretching increases.
- Carbonyl groups have two important resonance forms:



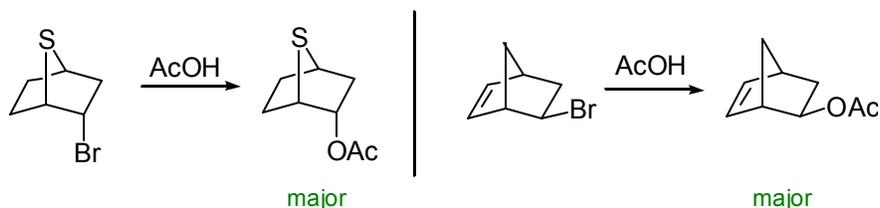
When structure II becomes a greater contributor to the resonance hybrid (the true electronic structure of the molecule), the IR maximum will shift lower-in-energy because the C=O bond will have less double bond character. The main factor governing the stability of structure II is stability of the carbocation.

- As the alkane rings become smaller, the C–C bond angles decrease. This means that to achieve the small bond angles in the strained rings, the orbitals involved in forming the C–C bonds must have more p character than a “normal” C–C aliphatic bond (sp³, bond angle = 109.5°).
- It follows from conservation of atomic orbitals when forming molecular orbitals that the bonds to the ring substituents will have more s character than typical aliphatic bonds. As s orbitals are lower-in-energy relative to p orbitals of the same shell, we would expect the carbonyl bonds with more s character to be stronger/stiffer, resulting in the observed trend in the IR data. An alternate approach to viewing this concept is that as s orbitals are more penetrating (they place e⁻ density closer to the nucleus) than p orbitals, the positive charge in resonance form II would be placed unfavorably closer to the positively-charged nucleus of the carbon atom. This effect is more pronounced as the rings become smaller, resulting in the carbonyl groups of the more strained ketones having more double bond character and thus stiffer bonds. Acetophenone exhibits lower energy absorption because the carbocation is in a benzyl position, where it is resonance stabilized. Thus, resonance form II becomes a greater contributor to the true electronic structure of the molecule.

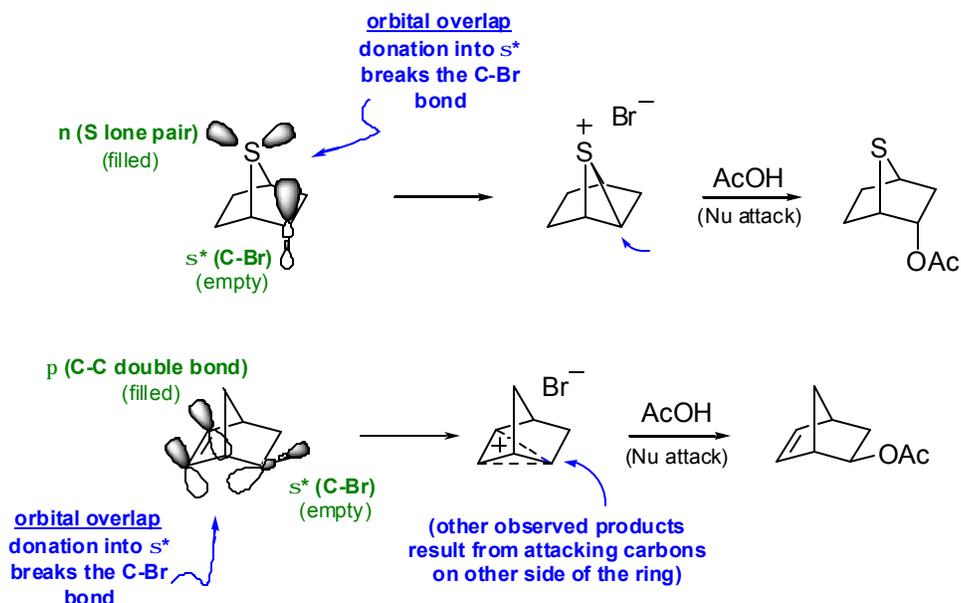
Key Lessons

- Pay attention to the subtle effects involved in hybridization and bonding, which often have profound macroscopic consequences

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.