Cyclopropyl Disrotary Ring Opening Reactions

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This study examines the cyclopropyl disrotary ring opening reactions shown in Figure 1.

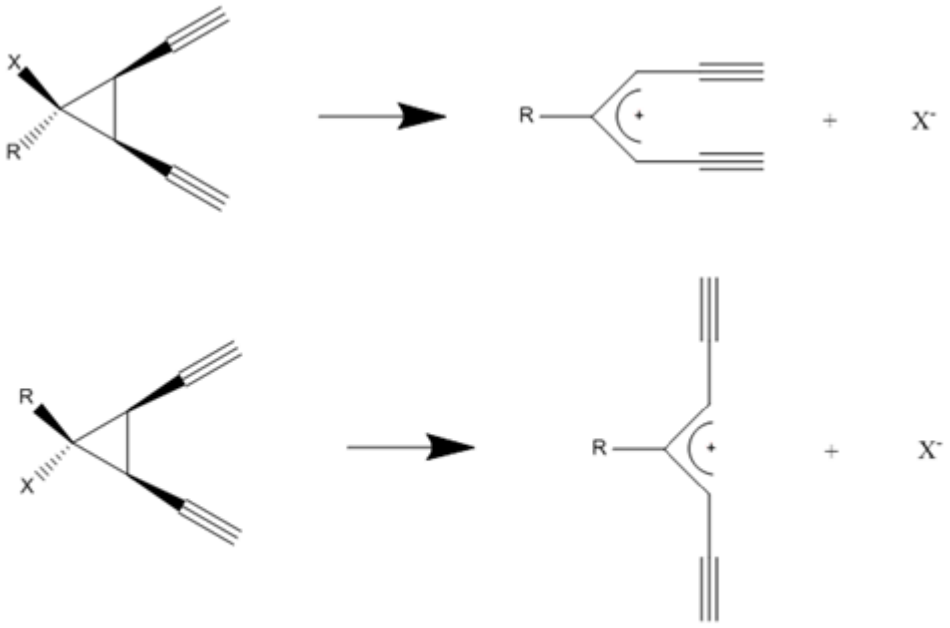

Figure 1. Cyclopropyl disrotary ring opening reactions

Depending on the stereochemistry of the molecule and placement of the "X" leaving group, the cyclopropyl ring will open into either the endo, endo (top reaction) or exo,exo (bottom reaction) acyclic molecule. The endo, endo structure is oriented ideally to undergo a Bergman cyclization to form a homotropylium diradical whereas the exo, exo structure is not likely to undergo such cyclization. We studied the energetics of the cycloproyl ring opening reaction with two different X-groups (H and CH_3) and three different R-groups (Cl, OH, and I). The geometries were optimized using the BLYP, B3LYP, and MPWB1K methods, and single-point QCISD/6-311++G** calculations were carried out using the B3LYP/6-311++G** results. The basis sets used were 6-31G* and 6-311++G** for calculations involving H, C, O and Cl. For I, the LANL2DZ and LANL2DZdp basis sets were used. The reaction energies and barrier heights for the two reactions were compared among methods and basis sets, as were the C_2-X bond lengths for reactant and transition state structures and C_2-C_1-C_3 bond angles for transition state structures.