

A density functional study of the Claisen rearrangement of allyl aryl ether, allyl arylamine, allyl aryl thio ether, and a series of meta-substituted molecules through reactivity and selectivity profiles

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The Claisen rearrangement of allyl phenyl ether, allyl phenylamine, and allyl phenyl thioether, together with the family of H, CH₃, OCH₃, Cl, F, and CN, meta-substituted molecules, is studied within a density functional framework with B3LYP exchange-correlation energy functionals and 6-311G** basis set. Reactants, intermediates, and products have equilibrium configurations (with no imaginary frequency), and the two transition states possess one imaginary frequency each corroborating the proposed mechanism of a [3,3]-sigmatropic rearrangement. The energy profile for the systems containing oxygen and nitrogen atoms mirrors the hardness profile along the reaction path in agreement with the maximum hardness principle. However, the molecules with sulfur atom do not follow the maximum hardness principle. This is explained in terms of the participation of the highest occupied molecular orbital (HOMO) in the reaction. The minimum polarizability principle is obeyed in all cases.