

The mechanism of Claisen rearrangement of allyl phenyl ether from the perspective of topological analysis of the ELF.

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The Claisen rearrangement of allyl phenyl ether to 6-(prop-2-en-1-yl) cyclohexa-2,4-dien-1-one has been studied by means of Bonding Evolution Theory (BET), which combines the topological analysis of the electron localization function (ELF) and catastrophe theory. The reaction can be presented as consisting of 10 main steps separated by fold and cusp catastrophes. The description of the mechanism of C-O bond breaking is complicated and depends on the DFT method used. It proceeds through a heterolytic cleavage (B3LYP, M052x) with the formation of the V-3(O) non-bonding basin in step II (M052x) or with electron density resonating between oxygen and carbon atoms in step II (B3LYP). The C-C bond between the allyl group and the phenol ring is formed after the TS in step VIII. The reaction is terminated by the formation of two localized CQC bonds in the phenyl ring in steps IX and X. The localization of $V_{i=1,2}(C,C)$ basins - typical of localized double bonds - in the phenyl ring proves the process of dearomatisation. The electronic structure of the transition structure distinguishes the non-bonding electron density concentrated in the vicinity of the C2 atom, represented by the $V(C2)$ basin, with a population of 0.28e. This basin is a "bridgehead" for the "construction" of the C-C bond between the phenyl ring and the allyl group.

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