

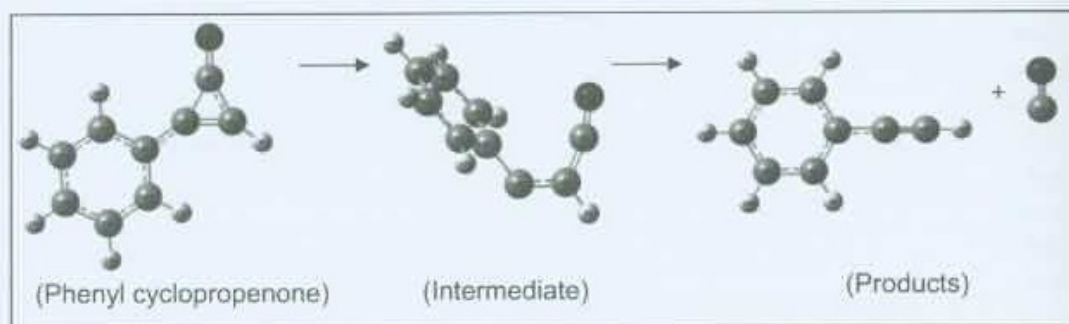


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Computational investigation of thermodynamic and kinetic feasibilities of cyclopropenone decarbonylation mechanism

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Since the first synthesis of cyclopropenone derivatives, there has been a great deal of interest in the chemical and physical properties of this class of molecules. Cyclopropenone on irradiation loses carbon monoxide and acetylene is produced in a very clean reaction. Although this decarbonylation reaction is a versatile tool in synthetic organic chemistry, little information is available regarding its mechanism. In this research, the substituent effect, the solvent effect and the mechanism of decarbonylation of cyclopropenone derivatives have been computationally studied using the Gaussian 09W; B3LYP hybrid function with the 3-21G basis set in a Linux operating system.



The substituent effect on cyclopropenone decarbonylation mechanism indicates that electron withdrawing substituents on cyclopropenone ring enhance the thermodynamic feasibility of the decarbonylation, whereas the trend is opposite when electron donor substituents are available. Solvent phase studies reveal that the decarbonylation reaction is more thermodynamically feasible in moderate polar solvents rather than in polar and non-polar solvents. Using TS Bery method based computational studies, transition states and intermediates of the phenyl cyclopropenone decarbonylation mechanism have been energetically located successfully. Since the decarbonylation of cyclopropenone containing 8-membered cyclic enediyne precursor was a thermodynamically non-spontaneous reaction, photo-irradiation can be used to generate the corresponding enediyne. This concept can be used to develop photo-switchable anti-tumor agents.