

"Cascading 1,3-Dipolar Cycloadditions: Combined and Consecutive Mechanisms to Azirines up to Pentazenes and Pentazoles"

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As specific needs arise, "click chemistry" reactions will inevitably depart from the goal of simple reactions to more complicated adaptations. As reactant azides or product triazoles become no longer suitable to an objective, replacement 1,3-dipoles will be sought, opening up possibilities for rearrangement. Indeed, encountering unexpected rearrangements often involving multistep cascades subsequent to cycloadditions is a significant feature of the synthetic versatility of the original Huisgen 1,3-dipolar cycloaddition reaction. Two general examples are given:

1) The reaction surfaces leading to rearrangements and ring expansions of azapentalene cycloadducts of imidazo- and triazolodicyanomethanide 1,3 dipoles with alkynes alkenes are studied with the (U)B3LYP DFT method. The surprisingly complex surface involves i) combined coarctate steps within one transition state but only consecutive pericyclic steps, and ii) anchimerically assisted H atom transfer competing with concerted symmetry allowed sigmatropic steps, all leading to or avoiding azirines, nitrenes, ylides, ionic, and assisted intermediates.

2) The pathways for the reaction of aryldiazonium cations plus azide anion to arylazide plus nitrogen are explored using the B3LYP/6-311+G(d) method. CCSD(T) calculations were performed on the HN₅ counterparts to verify the appropriateness of this DFT method to cases involving NN bond breaking. As in our prior MP2/6-31G(d) study, a pathway to direct formation of arylpentazole in a concerted reaction was not found, whereas transition states were found for the initial formation of three configurations of arylpentazene. Transition state structures were calculated for the pseudoelectrocyclic reaction of 21 E,Z arylpentazenes to pentazoles and for the loss of nitrogen from the pentazenes and pentazoles. Correlations were found between activation energies and both reaction energies and Hammett values for phenyl and 21 aryl substituted N₅ cases. The activation energies for competing cyclization and N₂ loss from E,Z pentazenes were both *ca.* 4 kcal/mol. The barriers for loss of N₂ from E,E and Z,E pentazenes are both *ca.* 20 kcal/mol. The lowering of the barriers in the E,Z configurations is attributed to the nucleophilic assistance of the in-plane lone pair on the N1 atom.