

Dissociative Electron Transfer of Phenyl-Substituted Bicyclic Endoperoxides

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Endoperoxides are compounds containing an O-O bond within a cyclic structure. In our laboratory, we study the electron transfer (ET) chemistry of such compounds using heterogeneous and homogeneous electrochemical techniques. Previous studies of aliphatic bicyclic endoperoxides, chosen as models for biologically important endoperoxides, revealed that ET occurs by a concerted two-electron reduction (Robert L. Donkers and Mark S. Workentin. *Chem. Eur. J.* **2000**, 7, 4012-4019). These studies also illustrated a methodology for determining previously unknown thermochemical information using Savéant's dissociative ET model; however, little insight was gained about the mechanistic details following ET. We have now begun a detailed study of bicyclic endoperoxides with aryl substituents on the bridgehead carbons. The incorporation of aryl substituents opens up the possibility for ET to occur by a stepwise reductive mechanism. This presentation will highlight the results for the bicyclic endoperoxides 1,4-diphenyl-2,3-dioxabicyclo(2,2,2)oct-5-ene (**1**) and 1,4-diphenyl-2,3-dioxabicyclo(2,2,1)heptane (**2**).

