

TITLE

Redox Reaction Initiated Homolytic and Heterolytic Coupling of Activated and Unactivated Olefinic Substrates Electrochemical Analysis and Synthesis

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The cathodic electrochemical behavior of the 2-Benzyloxy-1-methylpyridium triflate salt (**1**) in the presence or absence of methyl iodide, *cis*-cyclooctene and two monosubstituted malononitrile derivatives was studied in acetonitrile containing either 0.1 M [NBu₄][SO₃CF₃] or [NBu₄][PF₆] as the supporting electrolytes. Cyclic voltammetry (CV), square-wave voltammetry (SWV), and differential pulse voltammetry (DPV) and controlled-potential electrolysis were employed to investigate redox behavior of these compounds at glassy carbon and Pt disk electrode materials. A cathodic reduction of **1** gives rise to a single irreversible cyclic voltammetric wave at $E_{pc} = -1.82$ V versus Ferrocene/Ferrocenium couple (Cp₂Fe^{0/+}). These voltammetric processes are suggested for the rapid and efficient conversion of **1** into benzyl radical source. When a potential of -1.82 V (vs Cp₂Fe^{0/+}) is applied to a solution of **1** under standard conditions at room temperature, the compound **1** undergoes a two-electron reduction and yields bibenzyl (BB > 40% conversion) and toluene (> 10%) based on GC-MS analysis with external calibration curve data of BB and toluene. These could form *via* homolytic and heterolytic benzyl radical coupling reactions. In the presence of methyl iodide and **1** under identical conditions, it produces benzyl iodide (> 55%), ethylbenzene (<5%), bibenzyl (>20%), and toluene (> 10%). Products for these coupling reactions were identified by GC-MS and/or ¹H NMR data. Redox potentials of two monosubstituted malononitrile derivatives will be reported. The electrochemical reactivity of **1** with four additional substrates and mechanisms of these reactions will be discussed.

Biography

Daesung Chong was born in Chongup, Korea, in 1971 and received his B.S. from Kyonggi University, Korea, (1996) and his M.S. and Ph.D. from Sogang University (with C. S. Chin, 1998 and 2001) and did postdoctoral work at the Texas A&M University at College Station with Marcetta Y. Darensbourg and at the University of Vermont with William E. Geiger before joining the Electrochemistry researcher at Dow Corning Corporation in 2008. In 2010 he moved to the Ball State University in Muncie, Indiana. His main interest has been in the use of electrochemistry in analysis, synthesis and catalysis. His current research activity is to develop organic and inorganic synthetic methods under mild conditions with an electron that facilitate the efficient preparation of homogeneous (C-C) and heterogeneous (C-Si) coupling products from trivial and unactivated starting materials.