

Electrooxidative Coupling of Aromatics and Silyl Enol Ethers: Application to the Synthesis of Annulated Aromatics

Jeffrey B. Sperry* and Dennis L. Wright
Dartmouth College

Department of Chemistry, Dartmouth College, Hanover,
New Hampshire 03755

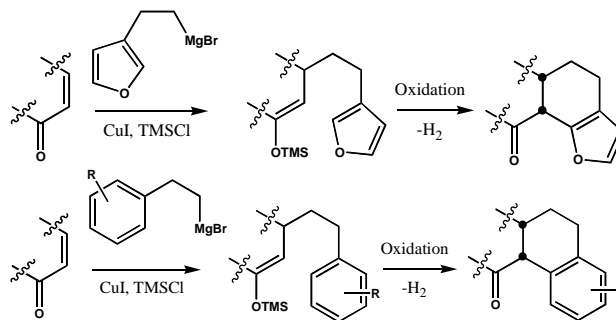
The preparation of annulated furan and benzene systems from a two-step conjugate addition, electrochemical annulation sequence has been studied. Trapping of the conjugate addition product as a silyl enol ether provides the precursor for the electrochemical ring closure (Scheme 1). We have shown that electron rich aromatics, such as furans and anisole derivatives, work well with the formation of six membered rings. The ring closure was highly stereoselective, leading to the formation of *cis*-fused systems.

To demonstrate its synthetic usefulness, a variety of functional groups were incorporated into our model study. Each studied functional group (carbamate, acetal, ester, isolated olefin, and aryl ether) was tolerated by the electrochemical ring closure.

To gain a mechanistic insight into the electrochemical ring closure, cyclic voltammetry and probe molecules were used. Oxidation adjacent to cyclopropanes and cyclobutanes to form cyclopropyl and cyclobutyl carbinyl radical cations permitted us to conclude that the initial oxidation occurred first at the silyl enol ether. Examination of the oxidation potentials of the model substrates also clearly showed the initial oxidation occurs at the silyl enol ether. Typical oxidation potentials for silyl enol ethers were 0.85-1.00V whereas the oxidation potential for similar furans occurred at 1.30V (Scheme 2).

Future work includes application of this strategy to the total synthesis of biologically active natural products. Current targets are hamigerin A, sarcodictyin A, and phomactin A.

Scheme 1.



Scheme 2.

