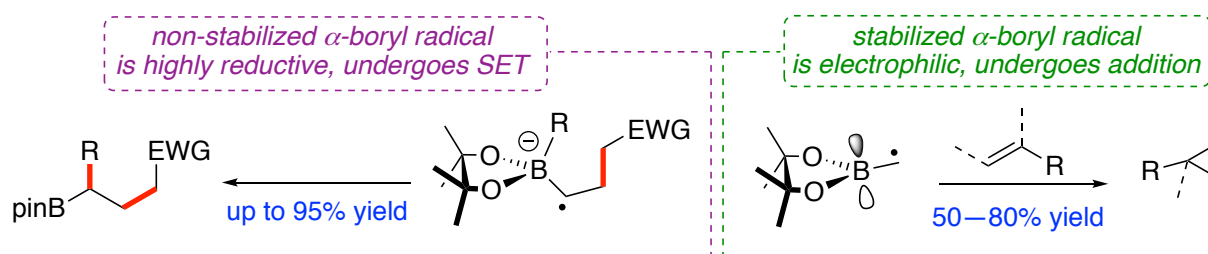


Reactivity and synthetic utility of α -boryl carbon centered radicals: two opposing reaction manifolds

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The vacant boron p-orbital in organoboranes has a stabilizing influence on a radical formally located on an adjacent carbon atom.^{1,2} The stabilized radical precursor ICH₂Bpin performs atom transfer radical addition (ATRA) to alkenes to furnish γ -iodoboronic esters. In an alternative manifold, occupying the vacant p-orbital on vinylboronic esters with a ligand eradicates any stabilization, and generates an excellent trap for electrophilic radicals.³⁻⁵ This time the mechanism operates through a single electron transfer (SET).



Our investigations concluded with two operationally simple, one-pot protocols; an ATRA/ 1,3-cyclization to yield cyclopropanes or a three-component coupling reaction of an organolithium, electrophilic halide, and vinylboronic ester. The scope, mechanism, and chemoselectivity of these two α -boryl radical chain processes will be discussed.

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