

DEANTIAROMATIZATION AS A DRIVING FORCE IN AN
ELECTROCYCLIZATION OF CYCLOPENTADIENONE AND
THE TOTAL SYNTHESIS OF 1-*epi-seco*-PSEUDOPTEROXAZOLE

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ABSTRACT

Deantiaromatization has been successfully demonstrated as a driving force in an electrocyclization of cyclopentadienones. The reaction was found to be general for a number of substrates and provides a unique way to access tricyclic ring systems with high stereoselectivity. Some evidence was uncovered to show that the process is indeed an 8π conrotatory electrocyclic ring closure.

During the exploration of substituent effects in the electrocyclization, a novel coupling reaction of an organolithium with primary halides was discovered. The experimental data suggested the engagement of the silicon atom and the important role of terminal alkene in the coupling reaction. However, the application of this methodology to other silane systems was successful.

The total synthesis of 1-*epi-seco*-pseudopteroxazole was accomplished in 17 steps, featuring the Buchwald-Hartwig coupling, a stereoselective intramolecular Michael reaction, a Heck coupling and asymmetric reduction of trisubstituted alkene.

In the course of reductive cleavage of the C-I bond to access key intermediate **358**, a novel dephenylation of Harmata benzothiazines was discovered to provide chiral cyclic

sulfinamides with complete stereocontrol. Preliminary mechanistic studies were carried out and a plausible mechanism was proposed based on our experimental results.