Stereoselective Intramolecular Carbolithiation of Olefinic α Lithio Amines

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STEREOSELECTIVE INTRAMOLECULAR CARBOLITHIATION OF
OLEFINIC α LITHIO AMINES

A Thesis
Submitted to the School of Graduate Studies and Research
in Partial Fulfillment of
the Requirements for the Degree
Master of Science

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Indiana University of Pennsylvania
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This thesis describes the investigation into asymmetric deprotonation of dipole-stabilized α-aminoorganolithiums. The lithiation of N-Boc-N-(3-butenyl)benzylamine provides a configurationally stable organolithium intermediates complexed to an oxygen atom. Preparation of heterocyclic rings is inhibited by this Li-O complex, therefore, restricting cyclization of unsaturated organolithium to form 5-membered rings.

However, the protection group on nitrogen plays a crucial role in the reaction topology, as an unexpected rearrangement occurred to provide for products that contained elimination abducts. An apparent 3-exo-trig cyclization occurs, followed by rapid and irreversible fragmentation of the strained 3-membered ring intermediate.

This led to the investigation of a variety of different substituent attached to the nitrogen in place of N-Boc. The conditions for the different substituent were probed at various temperature, bases, solvents, and ligands.