

1,5-HYDRIDE SHIFT OF ALKENYL SULFOXIMINE/ [4+3] CYCLOADDITION AND
RING OPENING/ NOVEL HYDRAZINE SYNTHESIS FROM TRÖGER'S BASE
ANALOGUES

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ABSTRACT

Three synthetic methodologies are studied in details in this dissertation.

For 1,5-hydride shift of alkenyl sulfoximine methodology, the reaction mechanism was studied using deuterium labeling. An uncommon 6-endo-trig 1,5-hydride shift process was discovered. The scope and limitation were studied using *N*-alkyl, *N*-allyl, and *N*-benzyl-substituted *S*-alkenyl sulfoximines. *N*-H-*S*-alkyl sulfoximines, four- and six-membered heterocyclic rings and a new class of chiral dienes were obtained.

In [4+3] cycloaddition and ring opening chapter, we demonstrated an ene-like reaction using a symmetric oxyallylic cation can provide α -substituted cyclopentenones. Enantio pure products are potentially accessible by this method. [4+3] Cycloaddition of the symmetric oxyallylic cation with substituted furans, and the ring-opening process of the resulting 8-oxabicyclo[3.2.1]oct-6-en-3-one were also studied. The reaction conditions and scope were investigated. An acid-catalyzed mechanism was proposed for the ring-opening process.

In the third chapter, we showed some interesting tetracyclic hydrazine compounds can be synthesized from Tröger's base analogues **1** by using the Polonovski reaction conditions. An oxidative rearrangement mechanism was proposed. Products were not obtained from some steric hindered Tröger's base analogues.