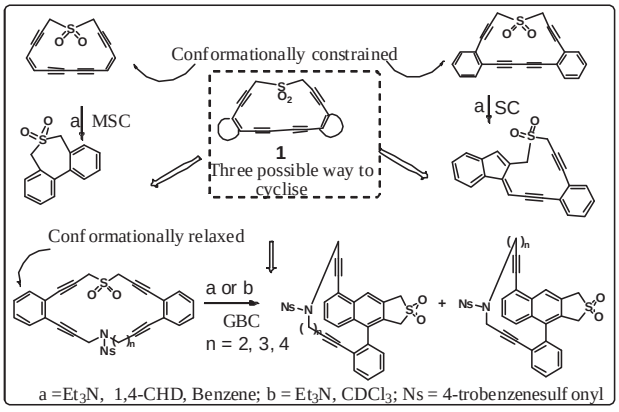
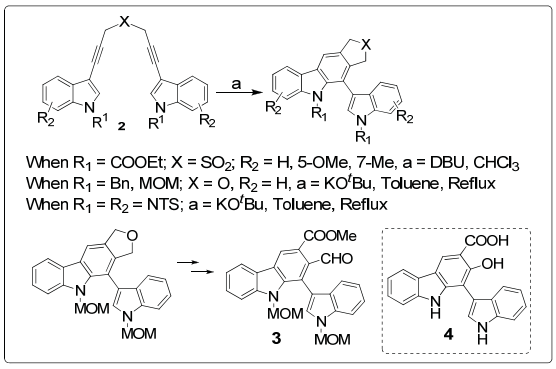
Abstract

STUDIES ON THE GARRATT-BRAVERMAN CYCLIZATION: ROLE OF CONFORMATION AND SYNTHETIC APPLICATIONS

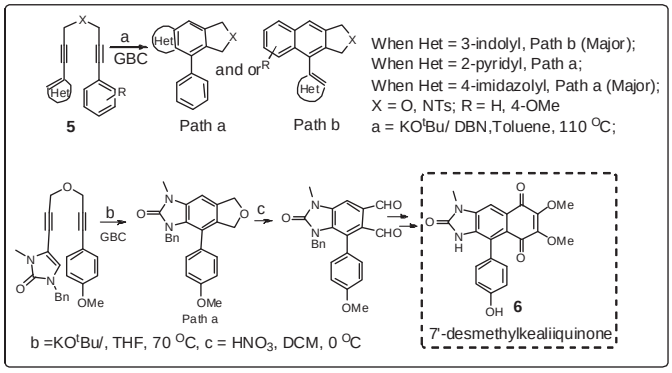
Nowadays the biology and chemistry of 1,4-diradicals are an important area of research as revealed by their ability of hydrogen atom abstraction from the DNA molecule and role in C-C bond forming reactions respectively. Myers-Saito (MSC) and Schmittel Cyclization (SC) give rise to such diradicals which need external sources like hydrogen atom donor for quenching. The Garratt-Braverman Cyclization (GBC) belongs to the self-quenching category and is the topic of interest of the present thesis. The first chapter contains a critical survey of diradical generating processes. We have reported the synthesis and reactivity of different conformationally constrained and relaxed *bis*-enynyl propargyl sulfones **1** in the second chapter. Under basic condition these sulfones capable of undergoing three parallel processes, namely, GBC, MS and SC (**Scheme 1**). The results have shown a general preference for GBC over MSC and SC; the preference can be reversed by applying conformational constraint. An explanation based on conformations comprising theoretical calculation has been put forward to explain the switchover. Third chapter describes a short synthesis of a wide array of carbazole and indolocarbazole skeletons present in several naturally occurring alkaloids involving GB Cyclization of various substituted *bis*-indolylpropargyl systems **2** as a key step.(**Scheme 2**). Furthermore applying this methodology an advanced intermediate aldehyde **3** was synthesised enroute to the total synthesis of pityriazole **4**. Lastly in the final chapter 4, we have studied the selectivity of GB reactions of unsymmetrical *bis*-propargyl ethers and sulphonamides **5** in which one of the terminal aryl groups is replaced by a heterocyclic ring (**Scheme 3**). Furthemore the result of selectivity was utilized in the synthesis of natural products of the kealiinine class **6**.



Scheme 1: Competition between GBC, MSC and SC



Scheme 2: Synthesis of indolocarbazole *via* GBC



Scheme 3: GBC of unsymmetrically substituted *bis*-propargyl ether and sulfonamides

Key wards: Garratt-Braverman, Myers-Saito, Schmittel, self-quenching, diradical, enynes, enyne-allenes, carbazole, indolocarbazole, kealiinine, kealiiquinone, natural products.