



Attemptd Synthesis of Cyclic Oxa-dieneynes for Studying Self-quenching Hopf Cyclization

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Abstract: In this paper I have reported an attempted synthesis of cyclic dieneynes having oxygen atom in cyclic framework and their reactivity study. I wanted to incorporate hetero atom (O) in different ways in the carbocyclic dieneyne framework. In type 1, one of the carbons present in the saturated chain is replaced by O atom. The intention was to explore the change towards Hopf cyclization temperature upon incorporation of heteroatom Oxygen in carbocyclic dieneyne framework. Another motivation was to explore the possibility of DNA cleavage by the intermediates for these oxa and aza Hopf Cyclizations as some of the intermediates may have sufficient half-lives so as to interact with external agents like biomacromolecules. Final ring closure reaction even in very high dilution condition resulted dimeric oxa-dieneynes instead of desired monomers and fails to cyclize under ambient conditions.

Keywords: Hopf cyclization, self-quenching, biradical, dimerization

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1. Introduction

In 1969, Hopf and Musso showed that hexa-1,3-dien-5-yne **1** undergoes a thermal cycloisomerization to give rise benzene.^{1a} The reaction starts above 274 °C, at which point isomerization between *E* isomer and *Z* isomer occurs. From a geometrical point of view, *Z* isomer is the reactive species which readily cyclizes and it is believed to proceed through the formation of a biradical intermediate followed by a H-shift resulting in the formation of benzene.^{1b} This cycloisomerization process is commonly known as Hopf Cyclization (HC).^{1a, b} In the Bergman Cyclization (BC)² of hex-3-en-1,5-diyne **6** the