PREFACE

Carbon-Carbon and Carbon-Heteroatom bond forming reactions occupy a central position in organic synthesis. Several carbon-carbon bond forming reactions have been discovered and their applications in organic chemistry have also been well developed. Recently, the Baylis-Hillman reaction, is yet another important reaction, has been added to the list of useful carbon-carbon bond forming reactions. The Baylis-Hillman reaction has attracted synthetic organic chemists in recent years because of its easy preparation and application in synthesis of densely functionalized molecules. These adducts have also been subjected to various transformations for the synthesis of important biologically active natural products.

The clay catalysts are known as eco-friendly acid catalysts which have potential for replacing the conventional mineral acids and are non-pollutant. The advantages of the clay-catalyzed reactions are that they are generally mild, solvent free and easy work-up.

Tin radical mediated cyclization has been developed as a potential method for preparing various types of carbocyclic and heterocyclic compounds via intramolecular carbon-carbon and carbon-heteroatom bond-forming processes.

In view of the growing interest in synthetic transformations of Baylis-Hillman adduct, we have carried out some investigations to explore the synthetic utility of Baylis-Hillman adduct using clay catalyst and vinyl radical cyclization methodology and the results are presented in the thesis entitled “Synthetic Application of Baylis-Hillman Adducts: Studies on Montmorillonite K-10 Clay Catalyzed and Tin Mediated Radical Cyclization Reactions”.

The thesis has been divided into four chapters. Relevant experimental and references are given at the end of each chapter.

We have used Baylis-Hillman adduct for the synthesis of $E$-Trisubstituted alkenes, Enyne ether derivatives and Indenes using Montmorillonite K10 clay catalyst. Further we have utilized the enyne ether derivatives for the synthesis of oxacyclic compounds by tri-butyltin hydride mediated vinyl radical cyclization methodology.

The chapter I has been divided into two parts. In the first part, a brief introduction about Baylis-Hillman reaction and its developments, synthetic transformations and applications in the synthesis of natural products have been outlined. In the second part,
introduction on clay catalyst with special emphasis on Montmorillonite-K10 clay and its application in organic synthesis are presented. A statement of the present research problem has also been incorporated at the end of this chapter.

Chapter II of the thesis deals with synthesis of E-trisubstituted alkenes and Indenes from Baylis-Hillman adduct. This chapter is divided into two parts for better clarity and understanding.

Part one deals with the isomerization of acetates of Baylis-Hillman adducts, a one- pot Protection-Isomerization of adduct with trimethylorthoformate and Nucleophilic substitution of Baylis-Hillman adduct with various alcohols under Montmorillonite-K10 clay catalyst.

Part two deals with Montmorillonite K10 clay catalyzed synthesis of Indenes through electro cyclic ring closure under microwave irradiation. Details about the synthesis of various hydroxy protected β-phenyl substituted Baylis-Hillman adducts and followed by synthesis of 1-aryl indenes using Montmorillonite-microwave combination are also presented. General information on the experimental procedure and characterization are also given at the end of this chapter.

A brief introduction to radical cyclization with a special emphasis on n-Bu₃SnH mediated vinyl radical cyclization and its applications are presented in chapter III.

The chapter IV deals with synthesis of Oxacycles from enyne ether derivatives of Baylis-Hillman adduct via vinyl radical cyclization. This chapter is sub-divided into three parts for easy understanding and clarity of the results.

Synthesis of trisubstituted tetrahydrofurans via 5-exo-trig vinyl radical cyclization is described in the first part. Part two deals with the stereoselective synthesis of tri and tetrasubstituted Tetrahydropyrans via 6-endo-trig and 6-exo-trig vinyl radical cyclization respectively. A stereoselective synthesis of Oxepanes via 7-endo-trig cyclization forms the subject matter of part three.

It may be noted that each chapters of the thesis is presented as a separate unit and therefore, Figures, Schemes, Tables and Structures are numbered accordingly. A summary of the work is given towards the end of the thesis.