Abstract
Over the years Claisen rearrangement has evolved as a powerful method in organic synthesis. Allyl vinyl ethers are the precursors for the Claisen rearrangement. So, methods for preparation of allyl vinyl ethers have acquired importance. Since once formed, almost certainly these ethers undergo Claisen rearrangement under thermal or Lewis acid catalyzed conditions. As a result several methods for their preparation have been reported in the literature. Each method has its own merits and demerits. Still there is a need to develop newer methods for the preparation of allyl vinyl ethers. The thesis describes efforts directed towards successful development of a method for the preparation of allyl vinyl ethers, their Claisen rearrangement, application of the rearranged products in the syntheses of natural products and a general method for cyclopentaannellation. The thesis is divided into three chapters

**Chapter-I : Wittig olefination route to allyl vinyl ethers-precursors for Claisen rearrangement.**

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\begin{align*}
\text{R}_1 & = \text{Alkyl or Aryl, R}_2 = \text{H or Alkyl, R}_3 = \text{H or CH}_3
\end{align*}
\]

This chapter describes the preparation and characterization of allyloxy and substituted allyloxy methylene phosphonium salts and reactions of the phosphoranes derived from these phosphonium salts with various carbonyl compounds. The chapter also describes the scope and the limitations for preparation of these type of salts.
Chapter-2: A general protocol for cyclopentaannellation.

This chapter describes the Claisen rearrangement of the allyl vinyl ethers, reported in chapter-1, to get substituted 4-pentenals. It further describes a short and efficient protocol for the construction and characterization of sterically crowded 2-cyclopentenones (scheme-1).

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\begin{align*}
\text{Compound} & & \text{R}_1 & & \text{R}_2 \\
1a & & \text{Ph} & & \text{CH}_3 \\
1b & & \text{p-Tolyl} & & \text{CH}_3 \\
1c & & [3,4\text{ di (OMe)-C}_6\text{H}_3]-\text{CH}_2\text{CH}_2 & & \text{CH}_3 \\
1d & & [4-(\text{OMe})\text{C}_6\text{H}_3]-\text{CH}_2\text{-CH}_2 & & \text{CH}_3 \\
1e & & 3,4\text{-(OMe)C}_6\text{H}_3 & & \text{H}
\end{align*}
\]

Claisen rearrangement of 1a-e in refluxing toluene furnished unsaturated aldehydes 2a-e. Wacker oxidation of 2a-e gave ketoaldehydes.
3a-e. Base catalyzed aldol condensation of 3a-e followed by dehydration afforded cyclopentenones 4a-e.

Chapter-3: Total synthesis of (±) laurenne, (±) epilaurenne, (±)α-cuparenone and β-herbertenol.

This chapter deals with the application of the methodologies, described in chapter-1 and chapter-2, in the syntheses of natural products. This chapter is subdivided into three sections

Section A: Total synthesis of (±) laurenne 5 and (±) epilaurenne 6 (scheme-2)

Wittig olefination of 4-methyl acetophenone with crotlyoxymethylene-phosphorane gave allyl vinyl ether 7 in 74% yield. Claisen rearrangement of 7 in refluxing toluene afforded unsaturated aldehyde 8 in 95% yield. Unsaturated aldehyde 8 under Wacker oxidation conditions gave ketoaldehyde 9 (82%)

(scheme-2)
which on base catalyzed aldol condensation followed by dehydration gave
cyclopentenone 10 in 90% yield. Hydrogenation of 10 gave cyclopentanone 11
in quantitative yields. A Lambardo reaction of 11 afforded an inseparable
mixture of the of the title compounds 5 and 6 in 80% yield.

Section-B : Total synthesis of (±) α-cuparenone 12 (scheme-3)

Enol ether 13 (E/Z mixture 1:1 ratio) was treated with prenyl alcohol in refluxing
toluene in presence of 10 mol% trifluoroacetic acid. This afforded unsaturated
aldehyde 15 (69%) via insitu generation of allylvinyl ether 14 followed by
Claisen rearrangement. Aldehyde 15, under Wacker oxidation conditions, gave
ketoaldehyde 16 (81%) which on base catalyzed aldol condensation followed
by dehydration yielded cyclopentenone 17 (87%). Hydrogenation of 17 afforded
(±)α-cuparenone 12 in quantitative yield.
Enol ether 19 (E/Z mixture 1:1 ratio) was treated with prenyl alcohol in refluxing toluene in presence of 10 mol% trifluoroacetic acid. This afforded unsaturated aldehyde 21 (64%) via *insitu* generation of allylvinyl ether 20 followed by Claisen rearrangement. Aldehyde 21, under Wacker oxidation conditions, gave ketoaldehyde 22 (79%) which on base catalyzed aldol condensation followed by dehydration yielded cyclopentenone 23 (86%). Hydrogenation of 23 afforded the cyclopentanone (93%) which on Wolff-Kishner reduction gave the title compound 18 in 32% yield.