ABSTRACT

The thesis consists of four chapters.

CHAPTER I - PHOTO-INDUCED VINYL CYCLOPROPANE-CYCLOPENTENE REARRANGEMENT: A LITERATURE SURVEY

The work presented in this thesis centres around the photo-induced vinylcyclopropane-cyclopentene rearrangement (photo-VCR, Eqn.1). Therefore, a brief survey of literature pertaining to this reaction has been outlined. The salient features of this reaction are highlighted to project the present work in proper perspective.

CHAPTER II - This chapter comprises two Sections.

Section A: NEW METHODOLOGY FOR THE SYNTHESIS OF BICYCLO[3.2.0]HEPTENES FROM CIS-METHYLVINYL CYCLOPROPANES

The success of VCR reaction under thermal conditions in the synthesis of cis-fused bicyclo[3.2.0]heptene system is confronted with a serious problem in the case of cis-alkylvinylcyclopropanes. This type of compounds instead of affording VCR products essentially, undergo a competing retro-ene reaction (Eqn.2). The work described in this chapter offers a solution to this problem in that various cis-alkylvinylcyclopropanes afforded exclusively the VCR products under sensitized conditions of irradiation.

Different 4α-substituted-2-carenes have been shown to furnish the corresponding 7-substituted-bicyclo[3.2.0]heptenes in good yields (Eqn.3). The products obtained have
been well-characterized on the basis of their spectral data and chemical correlations. The diastereomeric photoproducts have been assigned endo- and exo- configurations on the basis of PMR data. The study described in this chapter has resulted in a new methodology for the construction of cis-fused bicyclo [3.2.0]heptene derivatives.

The absolute stereochemistry of one of the epimeric alcohols obtained from the reduction of 4α-acetyl-2-carene has been determined as 1, from X-ray analysis.

Section B: STEREOCHEMISTRY-DEPENDENT REARRANGEMENT OF A HOMOALLYLIC ALCOHOL, 3

One of the products in the photolysis of 2 has been observed to undergo a rearrangement during its isolation by preparative GLC. The rearranged product has been characterized as 4 from its spectral properties. This rearrangement has been explained on the basis of stereochemically-dependent 1,5-sigmatropic hydrogen shift of the homoallylic alcohol 3.

CHAPTER III - SYNTHESIS OF GRANDISOL, 5 (A SEX PHEROMONE OF MALE BOLL WEEVIL)

The synthetic potential of the methodology described in Chapter II has been demonstrated by the synthesis of a key intermediate 7 of grandisol, 5, a major component of the sex pheromone of male boll weevil, a serious cotton pest. The principal reaction involved in the synthesis (Scheme I) is the toluene-sensitized photolysis of 2-carene 6. The other reactions employed have been depicted in the Scheme.
**Eq. 1**

\[
\text{Eq. 1: } \text{[reaction diagram with structures and labels]}
\]

**Eq. 2**

\[
\text{Eq. 2: } \text{[reaction diagram with structures and labels]}
\]

**Eq. 3**

\[
\text{Eq. 3: } \text{[reaction diagram with structures and labels]}
\]

R = OH, CH₂OAc, COOMe etc.

**cis-endo**

**cis-exo**

\[
\text{1}
\]
\[
\text{2}
\]
\[
\text{3}
\]
\[
\text{4}
\]
SCHEME - I.

\[ \text{6} \xrightarrow{\text{hv, Sens.}} \text{7} \xrightarrow{\text{mepba}} (\pm) \]

\[ \text{i) LAH} \xrightarrow{\text{ii) PCC}} \]

SCHEME - II.

\[ \text{8} \xrightarrow{\text{hv, CH}_3\text{OH}} \text{11} \xrightarrow{\text{}} \text{10} \]

SCHEME - III.

\[ \text{9} \xrightarrow{\text{hv, CH}_3\text{OH}} \text{12} \xrightarrow{\text{}} \text{13} \]
A preliminary investigation of photochemistry of the epimeric ketones 8 and 9 constitutes the subject matter of this chapter. The major product from the photolysis of endo-ketone, 8, has been tentatively assigned the structure 10 (Scheme II) on the basis of spectral data. This spiro alcohol 10 is supposed to have arisen from the N II cyclization of the primary photoproduct 11. Dihydroanalogue of this proposed intermediate 11 was synthesized by a ten-step sequence of reactions and its photolysis studied for the purpose of comparison.

The two products arising from N II cyclization from the photolysis of the exo-ketone 9 are characterized as 12 and 13 (Scheme III). Further support to the proposed intermediacy of 11 in the formation of 10 and characterization of the other minor products in the photolysis of 8 are in progress.