SUMMARY

Studies on carbene and ketene reactions have been submitted in three different parts of this thesis.

PART ONE

Studies on carbene reactions

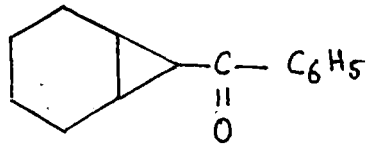
Chapter - I. Introduction to Carbene Chemistry

In this chapter history of carbene generation and a general introduction have been given at the outset. Next section of the chapter surveys different methods of carbene generation with special emphasis on keto carbene generation. Addition of ketocarbenes to olefins have been discussed and mechanisms of these addition reaction have also been cited. Subsequently a background survey of a few reactions involving cleavage and rearrangement of the cyclopropane ring system have been furnished.

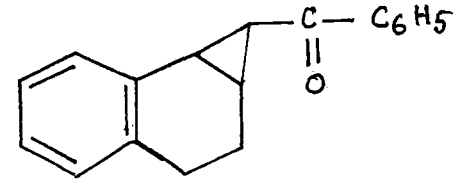
Theoretical aspects of the cases have been discussed briefly. The singlet and triplet states and structure of carbenes are discussed. Spectroscopic evidence and chemical evidences with reference to C-H insertion reactions and addition to C = C bonds have been described. Some factors influencing the reactivity of carbenes have been illustrated in this introductory discussion.

Chapter - II Cleavage of cyclopropane ring

In this chapter preparation of two cyclopropane derivatives via ketocarbene addition to cyclohexene (A) and to dihydronaphthalene (B) have been described.



[A]



[B]

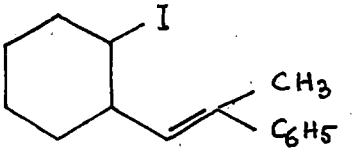
Cyclopropane adduct (A) on treatment with Grignard reagent (Methylmagnesium iodide) a Grignard adduct is formed which on acid treatment gave a homoallylic halide derivative (C). Compound (A) on treatment with phenyl magnesium bromide gave a Grignard adduct and this on acid treatment gave the compound (D). Action of vinylmagnesium bromide on compound (A) followed by acid treatment was studied when a solid compound (E) was found. Compound (C) on oxymercuration-demercuration reaction yielded an alcohol (F).

Methyl magnesium iodide treatment of (B) followed by acid treatment of the Grignard adduct thus obtained failed completely.

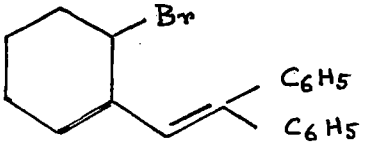
In a later section of this chapter discussions on the basis of the above experimental results and their

analysis, spectroscopic data such as IR, NMR and mass spectra are given.

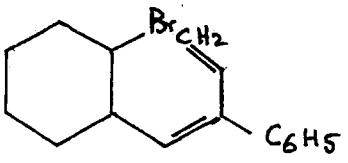
On the basis of analyses and spectroscopic studies the structures of the compounds (C), (D) and (F) have been established.



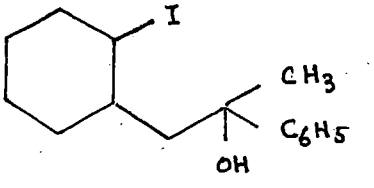
[C]



[D]



[E]



[F]

The last section deals with the experimental details of the reactions to obtain the above compounds.

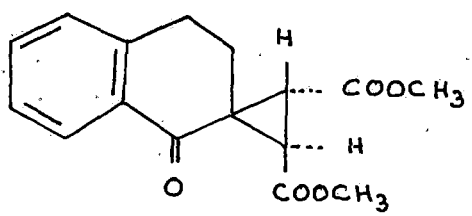
Chapter - III Decomposition of diazotetralone

In this chapter preparation of α-diazotetralone has been described. Ultra-violet spectral studies on the decomposition of α-diazotetralone were undertaken and concluded that the application of copper catalyst helps thermal decomposition of α-diazotetralone alone. But it has been found that thermal decomposition of α-diazotetralone in presence of copper catalyst and an olefin(substituted

cinnamic esters, methyl crotonate, cyclohexene etc) failed to give any cyclopropane adduct whereas dimerisation of α-diazotetralone was observed.

Reaction of α-diazotetralone with dimethyl fumerate in presence of catalyst (copper) and in absence of catalyst gave the cyclopropane adduct (G).

Structure of this cyclopropane adduct (G) was fully characterised by the help of analysis, IR, NMR and mass spectra and may be written as



[G]

Experimental details of these reactions have been described in the concluding part of this chapter.

PART TWO

Studies on Reactions of Diazomethane

Chapter - I A short review on diazomethane addition to olefin.

In this chapter a very brief survey only on the 1,3-dipolar addition of diazomethane with olefin and some cyclopropanation reactions of diazomethane with olefin have been described.

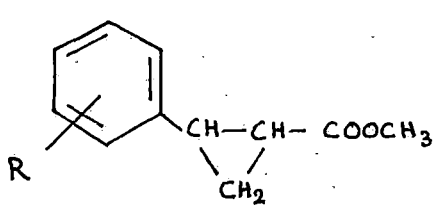
Chapter - II Reactions of diazomethane with some olefins

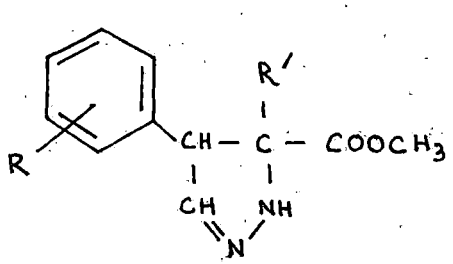
In this chapter reactions of diazomethane with some substituted cinnamic esters in presence of different catalysts have been described. Diazomethane on reaction with o-methoxy and p-methoxy cinnamic esters, both in presence of catalysts palladium acetate and uranyl acetate gave cyclopropane derivative (H) and (I) respectively in good yield.

Reactions of diazomethane in presence of same catalysts o-chloro, p-chloro, o-nitro and ∝-cyano cinnamic esters gave 2-pyrazoline (J), (K), (L), (M) respectively.

1-pyrazoline (N) and (O) were isolated in cases of reaction of diazomethane with trans-phenyl methyl cinnamate trans-naphthyl, o-chloro methyl cinnamate respectively in presence of same catalysts.

In the results and discussions section the characterisation with the help of analysis, IR, NMR and mass spectral data have been described and their structures have been proposed as follows.





(X)

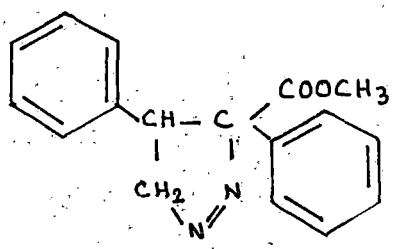
H, R = o-OCH_3 J, R = o-Cl, R' = H

I, R = p-OCH_3 K, R = p-Cl, R' = H

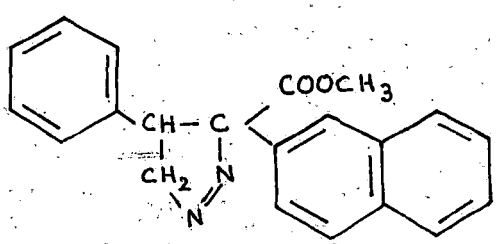
L, R = o-NO_2, R' = H

M, R = H, R' = CN

Structures of compounds (N) and (O) are assigned as follows



[N]



[O]

Experimental details are presented in the next section of this chapter.

PART THREE

Studies on Ketene Reactions

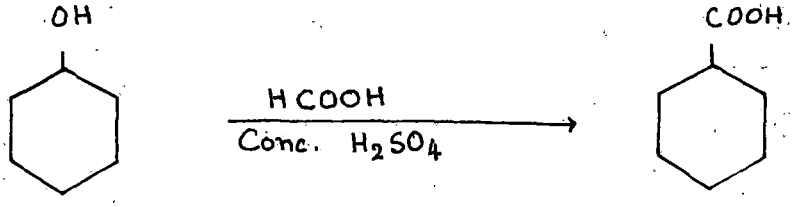
Chapter - I Review on Ketene Reactions

A short review on different methods of preparation of ketenes, their reactions with various compounds with special emphasis on addition reactions to olefins and carbonyl compounds producing cyclobutanone derivatives and oxetanone

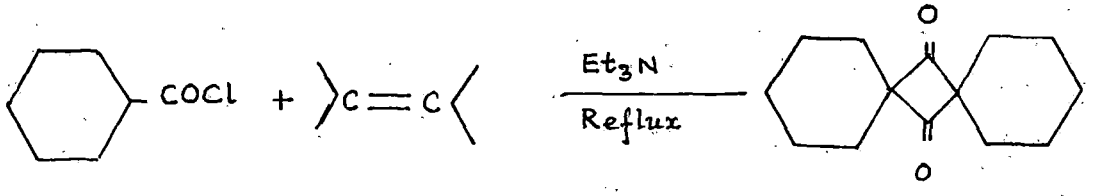
derivatives have been described in this chapter.

Chapter - II Reactions of Ketenes

In this chapter description of our attempts of preparing certain ketenes and their attempted reactions have been furnished. Cyclohexane carboxylic acid was prepared from cyclohexanol with formic acid and concentrated sulphuric acid. Then this acid was converted into its acid chloride. Dichloroacetyl chloride and trichloroacetyl chloride was prepared from the respective acids.



Cyclohexane carboxylic acid chloride on refluxing with different olefins in presence of triethylamine afforded dimer (P) only, other products could not be characterized.



[P]

Dichloroacetyl chloride on refluxing with olefin in presence of triethylamine, similarly, are unsuccessful completely. Here also dimer is the characterisable product.

Trichloroacetyl chloride was treated with activated zinc dust in presence of olefins and α-tetralone but these reactions also failed to yield any conclusive result.

Experimental details have been described in last part of this chapter.