SUMMARY

The work embodied in the present thesis has been divided into two parts.

PART-I

SOME STUDIES ON KETOCARBENES ADDITION TO DOUBLE BONDS AND RELATED REACTIONS.

Chapter-I:

In this chapter a short introduction to the Chemistry of carbenes is given.

Section-A:

This section gives a review of the historical background of the methylene (rather carbene) reactive intermediate.

Section-B:

This section gives a short review of the singlet and triplet state of the carbene.

Section-C:

This section deals with some of the general procedures of carbene generation.

Section-D:

This section attempts to record some of the factors affecting these reactions. These effects which come into play in the carbene reaction often play an important role. The effects are mainly due to electronic factors, steric factors and the effects due to the mesomeric and induction are discussed curiously.

Section-E:

This section deals with the nature of the transition state for C-H insertion and addition of Carbene to double bonds.

Chapter-II:

This chapter records some additional aspects of keto carbene reaction.

Section-A:

This section gives a short review on keto carbenes and their reactions.

Section-B:

This section gives some idea about the mechanistic pattern of keto carbene addition to double bonds.

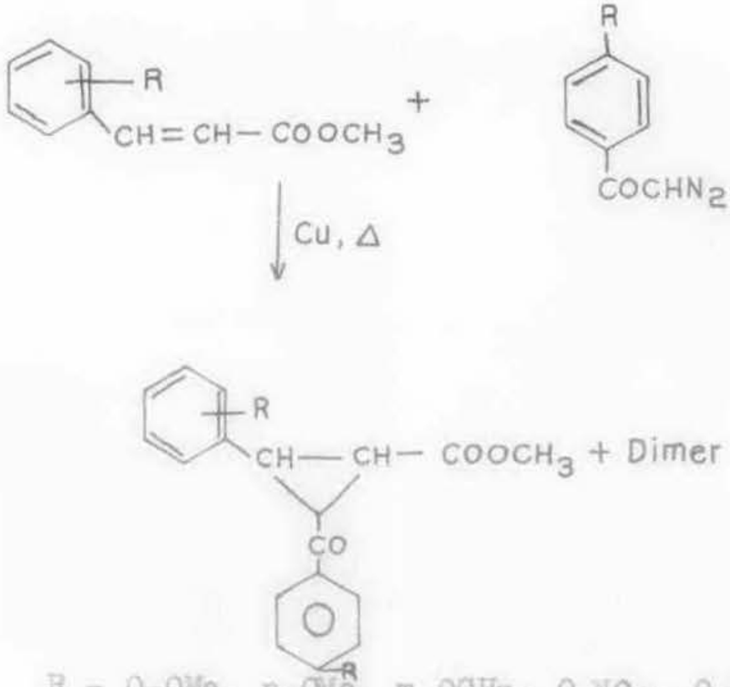
Chapter-III:

This chapter deals with the present studies on the reactions of diazoketones with some selected cinnamic esters.

Section-A:

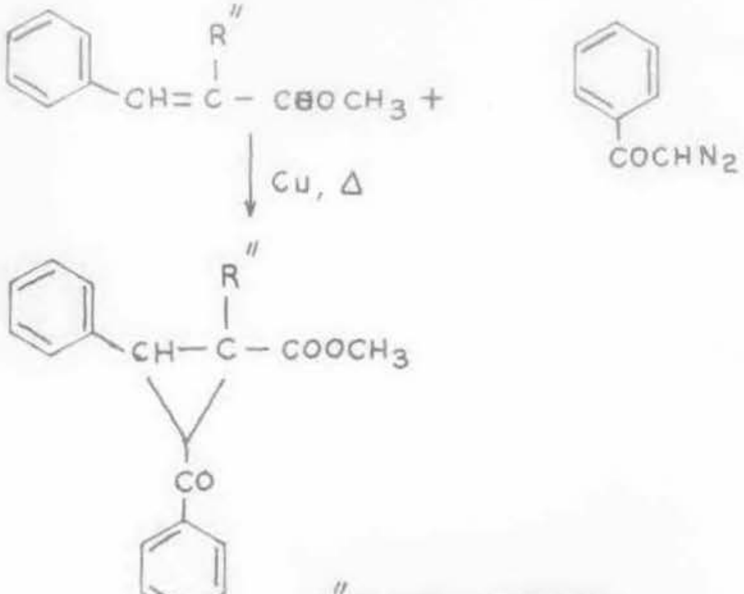
This section deals with the aims and objects of this study i.e. keto carbene addition to cinnamic esters. In this study various cinnamic esters, substituted in the ring at ortho, meta and para positions as also α-substituted cinnamic esters were taken. Whereas the diazo ketones used were α-diazoacetophenone, p-chloro-α-diazoacetophenone, p-methoxy-α-diazo acetophenone, p-nitro α-diazoacetophenone and α-diazoacetonaphthone. Reactions of these diazoketones and cinnamic esters are recorded.

The reactions may be written in the following way.



R = O-OMe, p-OMe, m-OCH$_3$, O-NO$_2$, O-Cl, P-Cl,
P-NO$_2$, O-COOCH$_3$ and H.
R' = P-Cl, P-OMe, P-NO$_2$ and H.

and also



R'' = -CN, - COOCH$_3$

A comparative study of the reaction of the diazoketones with these cinnamic esters has been made.

Section-B:

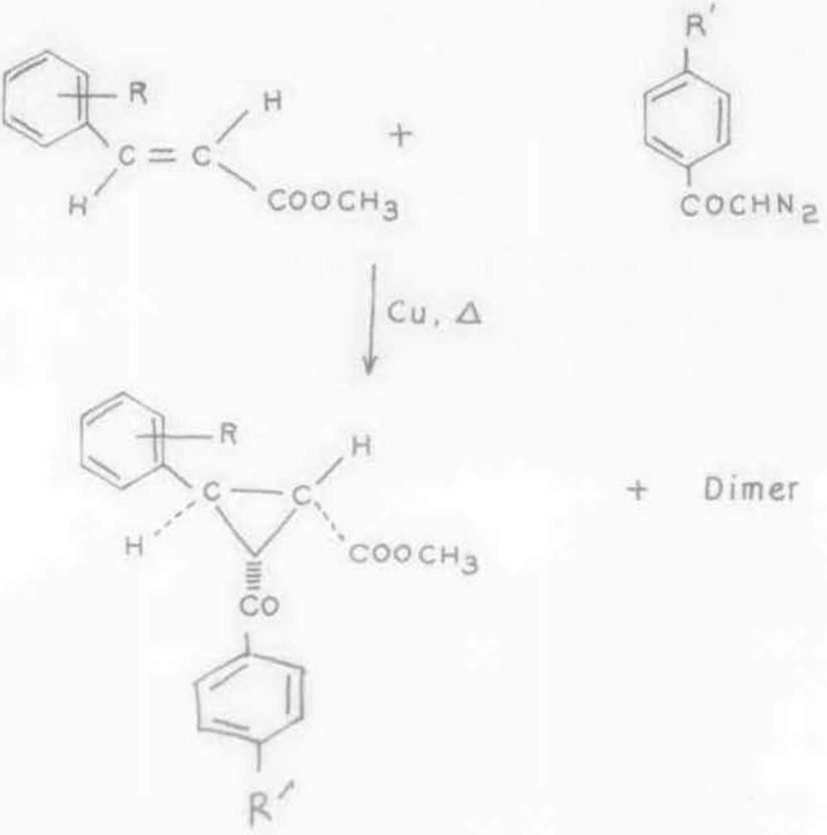
This section deals with the results and discussions of the reactions of diazoketones with cinnamic esters.

Reactions between diazoketones and cinnamic esters give rise to cyclopropyl ketones and dimer of the keto carbenes. But cyclopropyl ketones were not isolated in all the cases studied here.

O-methoxy and p-methoxy methyl cinnamate give rise to larger amount of cyclopropyl ketones. But p-nitro, p-chloro, o-carbomethoxy cinnamic esters do not give cyclopropyl ketones at all. Similarly when α-position of the cinnamic ester contains a carbomethoxy group does not give cyclopropyl ketone at all.

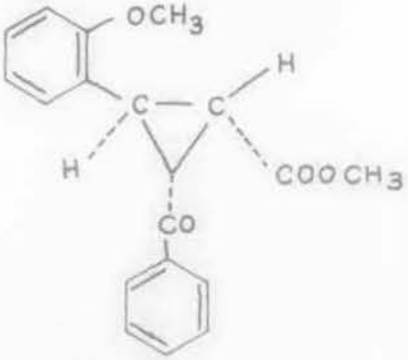
I.R. spectrum of these cyclopropyl ketones showed bands at 1010-1025 cm^{-1} indicating that these compounds contain a cyclopropane ring. I.R. spectra of these compounds also showed bands near 1700 cm^{-1} to 1720 cm^{-1} indicating that these compound contains an ester function also. Bands at 1655 cm^{-1} to 1680 cm^{-1} indicated the presence of carbonyl function in these compounds.

UV spectra showed peaks from 238 to 248 nm for these compounds which indicated that these compounds contained a phenyl group β to the aroyl function. This fact furnished easy evidence for the formation of a cyclopropane ring in these compounds. The studies indicate that the addition was a trans one in the case of trans esters and diazo ketones and we have isolated only one product.



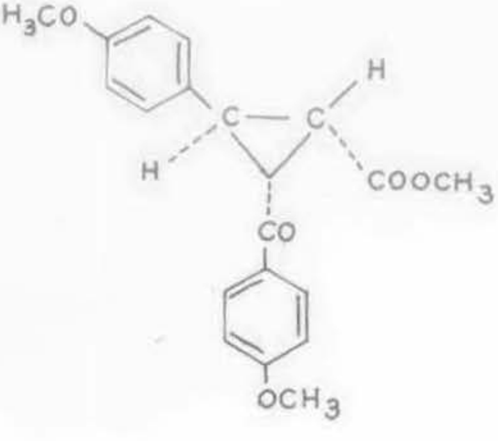
Mass spectrum of 1-benzoyl-2-carbomethoxy-2'-(o-methoxy) phenyl cyclopropane showed peaks at 295 ($M^{+}-OCH_3$), 238, 223, 205, 120, 118, 108, 105, 92, 77, 76, 64 and 44.

These peaks were explained as arising due to the following parent compounds:

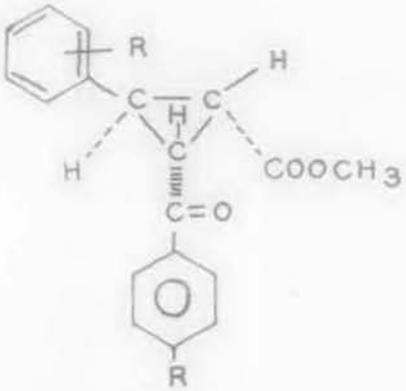


The mass spectrum of 1-(P-OCH_3) benzoyl-2-carbomethoxy-2'-(P-OCH_3) phenyl cyclopropane showed peaks at m/e 325 (M^+-OCH_3), 297, 188, 156, 135, 121, 108, 92, 75, 72 and 44.

These peaks were explained as arising due to the following structure:



The N.M.R spectra were also obtained and we made a comparative study of the N.M.R. signals of the starting esters and that of the reaction product. In all cases the reaction products did not show any N.M.R. signals at δ 6.22 to δ 6.43 ppm arising as due to simple olefinic proton indicating absence of olefinic double bond. A quasi doublet N.M.R. signals at δ 4.1 to δ 4.9 indicated that the cyclopropyl ketones were 1,2,2', a trisubstituted cyclopropane whose structure should be written in the following way.



In addition other signals due to different protonic absorptions were also noted.

P.M.R. signals at δ 3.9 to δ 3.95 indicating the presence of OCH_3 group attached to phenyl i.e. ether linkage. Signal at δ 3.8 indicating the presence of OCH_3 group of carbomethoxy group, The P.M.R. bands in the region of δ 6.9 to δ 7.5 indicated the presence of phenyl moiety and the N.M.R. bands in the region of δ 7.5 to δ 8.5 indicated the presence of benzoyl group.

These observations have been found in the reaction products of p-methoxy methyl cinnamate with α-diazoacetophenone and p-methoxy α-diazoacetophenone. Detailed P.M.R. records of the products from o-methoxy methyl cinnamate with p-methoxy α-diazoacetophenone and that of methyl cinnamate and α-diazoacetophenone are also recorded.

Section-C:

Experimental details of this chapter have been described in this section.

Chapter-IV:

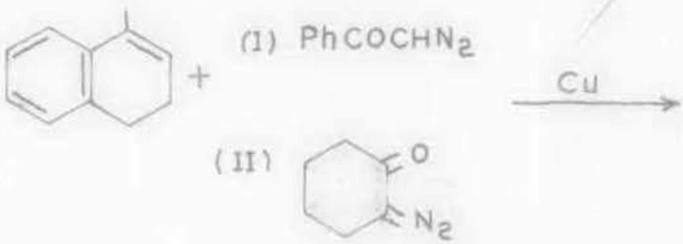
This chapter deals with the reactions of diazoketones with various other olefinic systems.

Section-A:

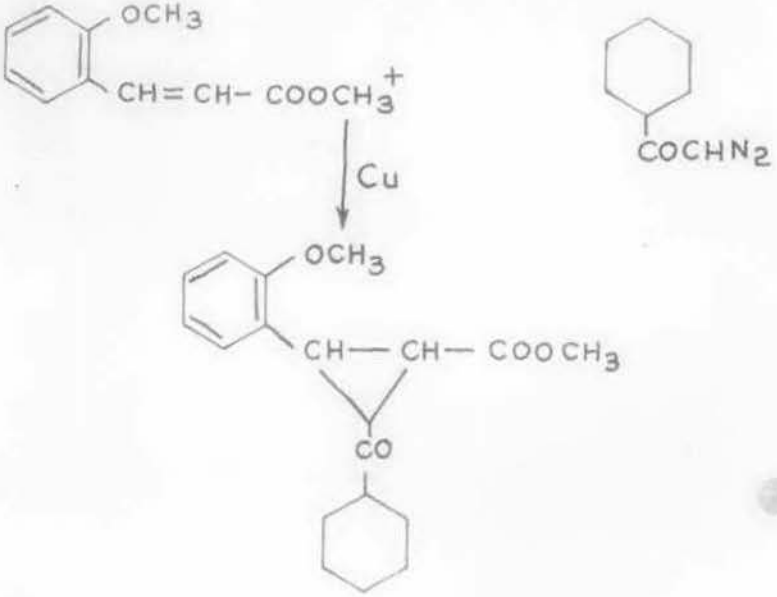
This section deals with the reaction of some diazo ketones other than α-diazoacetophenone with different types of olefinic systems other than cinnamic esters, in order to make a comparative study with that of the reactions which had been recorded earlier. In this connection, reaction of α-diazoacetophenone with methyl meth-acrylate and methyl crotonate were studied to see the effect of CH_3 group in the α or β position of methyl acrylate on the yield of cyclopropane derivative and it is observed that CH_3 group in the β position lowered the yield.

Reaction of cyclohexene with α-diazoacetophenone and α-diazoacetonaphthone were studied. The effect of the different keto carbenes and their steric hind~~e~~rance factor, on the yield of the cyclopropane derivative were made.

Reaction with diazo keto compounds with 3-4 dihydro α-methyl naphthalene were studied to see the steric effect exerted by this tri-substituted olefinic compound.



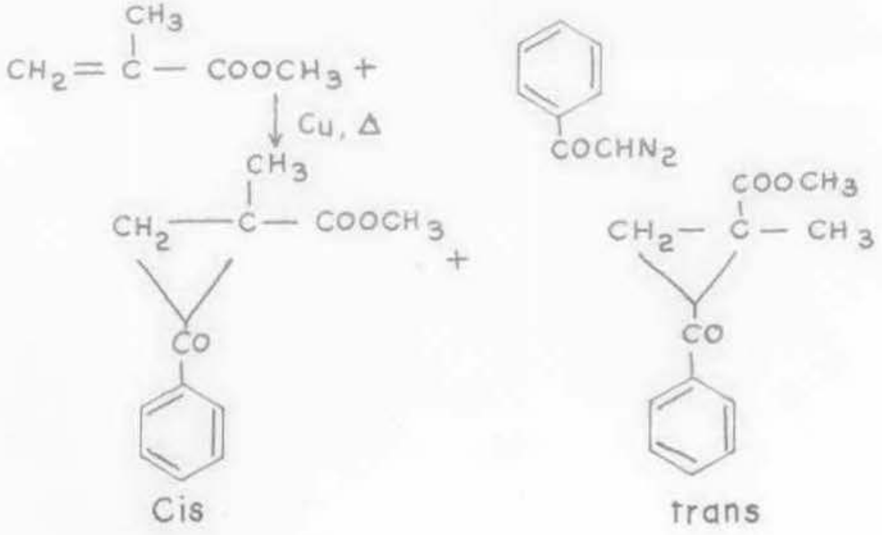
Reaction of o-methoxy methyl cinnamate and a diazo methyl cyclohexylketone was studied to see the effect of the aliphatic keto carbene on the yield of cyclopropane derivative to that of a aromatic diazo compound i.e. α-diazoacetophenone.



Section-B:

This section deals with the results of the reactions of diazo ketones and various olefinic systems involved in the previous section.

It was seen that CH_3 group when situated at the β position gave poor yield of the cyclopropane derivative than when it was in the α position of the methyl acrylate when reacted with α-diazoacetophenone in each. The structure of the reaction product of the α-diazoacetophenone and methyl methacrylate was confirmed by I.R., U.V. and N.M.R spectrum. Also G.L.C. showed that there were two products. The cis and trans adducts had been formed.



Reaction between cyclohexene with α-diazoacetophenone and α-diazoacetonaphthone showed that in the latter case, yield was poor and this is explained as due to the larger size of the keto carbene.

Reactions between α-methyl 3,4 dihydro naphthalene with diazo compounds were unsuccessful probably due to the tri substituted nature of the olefinic double bond. The reaction between α-diazo cyclohexanone with the olefinic double bonds also failed.

Reaction between an aliphatic diazo compound and cinnamic esters showed that it gave poor yield of cyclopropyl ketones.

The identification of these products were made by G.L.C. in the case of liquid product and the use of I.R., U.V. and elemental analysis made both in the cases of liquid and solid products.

I.R bands of some of the products at 1010 cm^{-1} to 1020 cm^{-1} indicated the presence of cyclopropane ring and band at 1655 to 1680 cm^{-1} indicated the presence of carbonyl group.

Section-C:

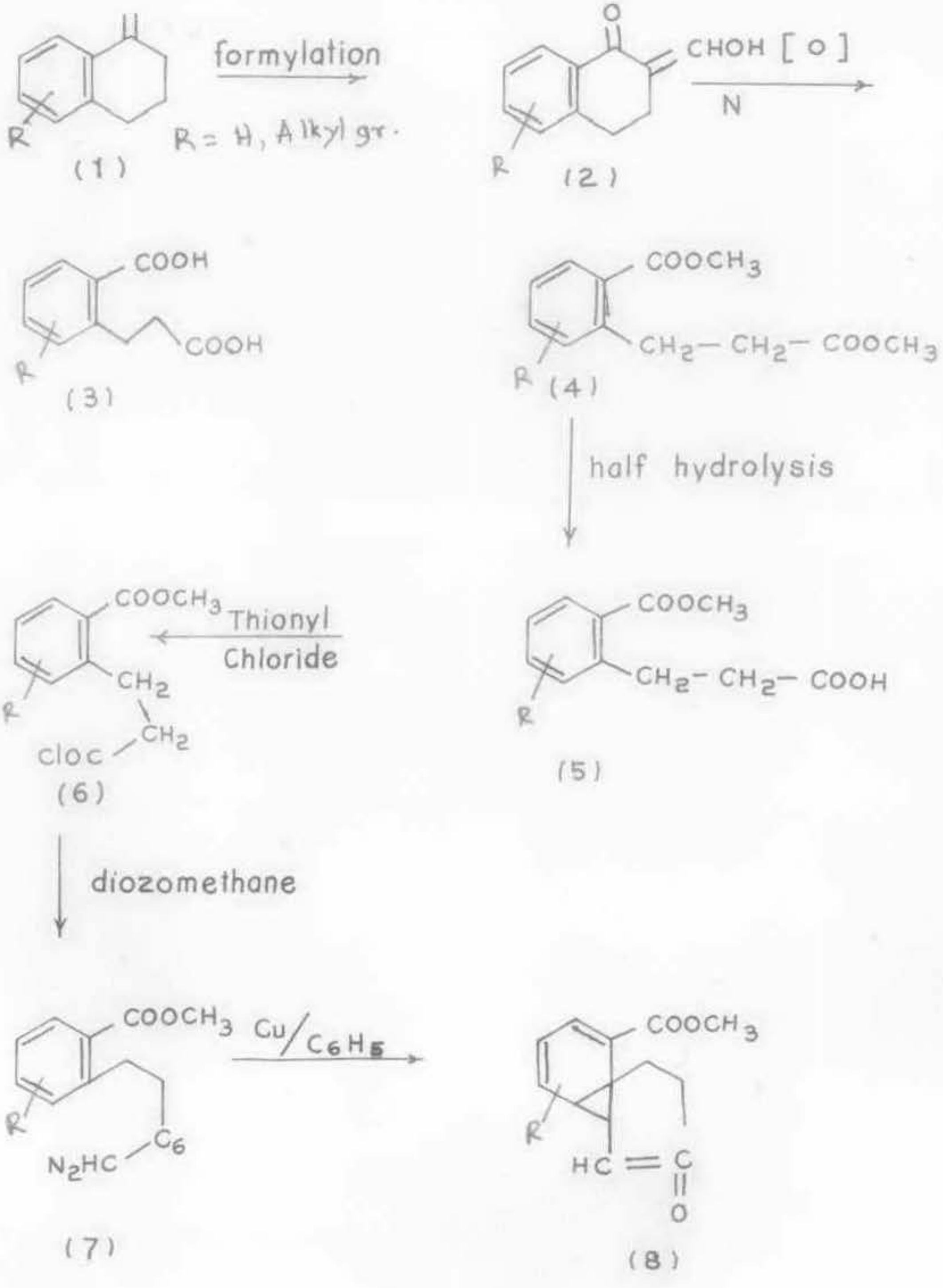
Experimental portion of this chapter has been described in this section.

Chapter-V:

This chapter deals with the intramolecular keto carbene addition to aromatic system.

Section-A:

In order to study the intramolecular keto carbene addition to some selected aromatic systems following reactions were attempted.

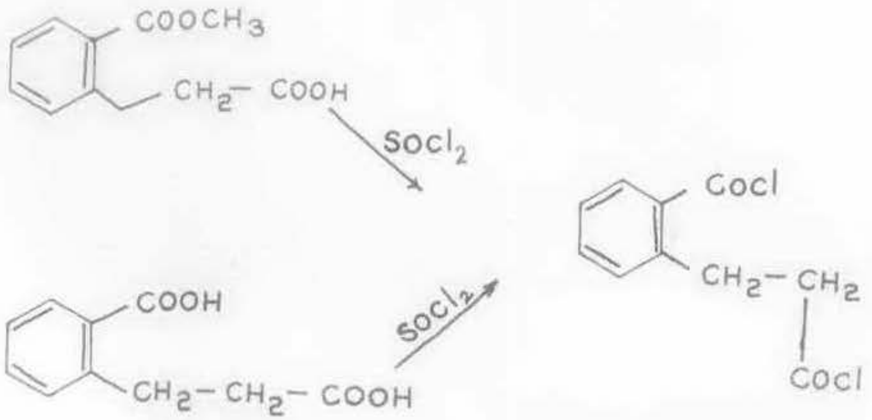


Section-B:

Formylation of α-tetralone gave hydroxy methylene (2) which on oxidation by $K9O_4/KMnO_4$ gave diacid [3] which was also prepared alternatively by oxidation with H_2O_2/CH_3COOH of β-naphthol. This on esterification gave diester [4] which on careful hydrolysis gave the half ester [5]. At this stage difficulty was experienced as [5] was treated with thionyl chloride diacid chloride [9] instead of [6] resulted. It was not possible to prepare [6]. The structure of [9] was confirmed to be the structure of the diacid chloride of the acid by the comparison of I.R. spectra.

The identification of the other compounds was done by elemental analysis and I.R.

Some cursory work to prepare [7] by alternative synthetic procedures have not as yet yielded fruitful results.



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Section-C:

Experimental portion of this chapter is described in this section.

Chapter-VI:

This chapter deals with the relative catalytic activity of some metal ions in the reaction of α-diazoketones.

Section-A:

In this section the metal ion activity of some Cu salts i.e. CuCl, $CuSO_4$ (anhydrous), Cu and palladium acetate on the yield of cyclopropyl ketones were studied when the reactants were p-methoxy methyl cinnamate p-nitro methyl cinnamate and α -diazoacetophenone maintaining all the other experimental conditions as identical as possible. It was seen that Cu gave maximum yield where as palladium acetate did not catalyse the addition reaction.

Chapter-VII:

This chapter deals with the effect of potassium tert-butoxide on cyclopropyl ketones.

Section-A:

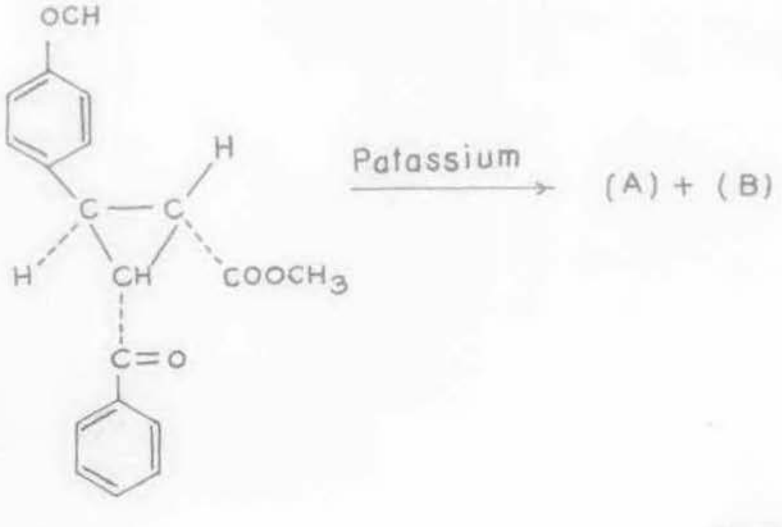
This section contains aims and objects of the above study. It is known that cyclopropyl ketones undergo different types of rearrangement when they are treated with liquid ammonia, perchloric acid, HCl and H_2SO_4.

It was an object to see what type of rearrangement took place when cyclopropyl ketones, prepared here, were treated with potassium-tert-butoxide. With this view 1-benzoyl-2-carbomethoxy-2'-(p-methoxy) phenyl cyclopropane was treated with potassium tert. butoxide.

Section-B:

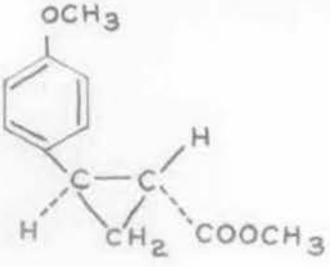
When 1-benzoyl-2-carbomethoxy-2'-(p-methoxy) phenyl cyclopropane treated with potassium t-butoxide gave two products, (A) and (B). (A) has been confirmed to be benzoic acid by elemental analysis, I.R, mass spectrum and also by the comparison of IR bands with that of benzoic acid.

The identification of (B) was done by elemental analysis. IR bands at 1010 cm^{-1} and 1700 cm^{-1} showed the presence of a cyclopropane ring and an ester function in this part. NMR spectrum in the region δ 1.2 to δ 2.5 showed the presence of cyclopropane hydrogens.



A =

The structure of B.



Section-C:

Experimental portion of this chapter has been described in this section.

PART - II

REACTION OF DIAZOMETHANE WITH CINNAMIC ESTERS.

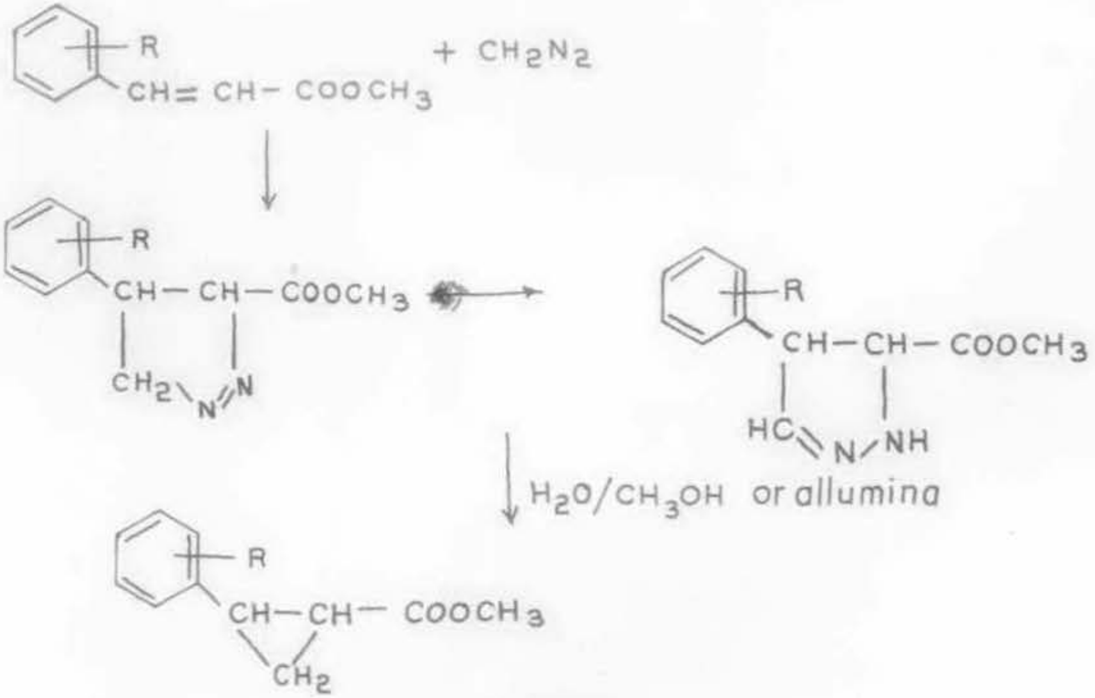
Chapter-I:

Section-A:

In this section a short review of the structure of diazomethane and 1,3 cyclo addition and various reactions of diazomethane with olefinic double bonds has been presented.

Section-B:

In this section the reactions of diazomethane with cinnamic ester in order to prepare 1 or 2-pyrazoline and thereby to prepare cyclopropane derivatives have been discussed.



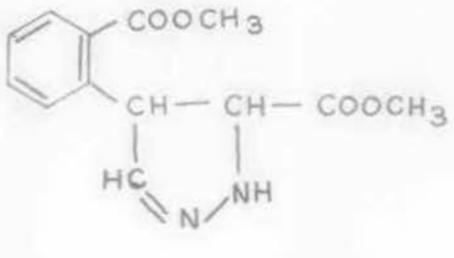
$R = O\text{-}Cl, O\text{-}NO_2, O\text{-}COOCH_3$

Section-C:

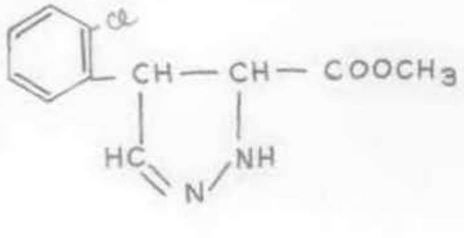
This section deals with the results and discussions of the reaction of diazomethane with o-chloro methyl cinnamate, o-carbomethoxy methyl cinnamate, o-nitro methyl cinnamate, p-nitromethyl cinnamate and mesityl oxide.

In most of the cases, 2-pyrazoline were isolated, whose structure were confirmed by elemental analysis, I.R., mass spectra and N.M.R spectra. In the case of liquid product G.L.C. was reported. IR spectrum in the region of 3300 to 3400 cm^{-1} of these compounds indicated the presence of secondary amine group.

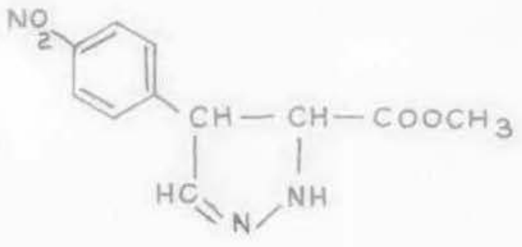
Mass spectrum of 3-carboxylate-4 (o-carbomethoxy)-2-pyrazoline showed peak at M^+(262) together with other peaks at Fig P14. These fragmentations could be explained arising to the following structure of the compound.



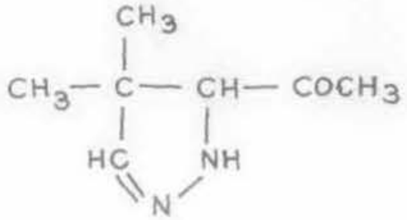
Mass spectrum 3-carboxylate-4 (o-chloro) phenyl 2-pyrazoline showed bands at M^+(232) and other bands. These fragmentations could be explained as arising due to the following structure:



This was further confirmed by N.M.R . N.M.R signals at δ 4.1 (broad) of 3-carboxylate-4 (p-nitro) phenyl 2-pyrazoline is accounted as due to the presence of NH proton. In addition it had signals due to $COOCH_3$ proton, phenyl proton, N - CH proton. All these observations were explained as arising due to the following structure of the compound.



Reaction product of diazomethane and mesityl oxide gave only one product as seen by G.L.C. This contained NH grouping. So the structure of this product is



These 2-pyrazoline when treated with alumina or CH_3OH or H_2O did not afford any cyclopropane derivative. So thermally 2-pyrazolines are more stable than 1-pyrazoline.

Section-D:

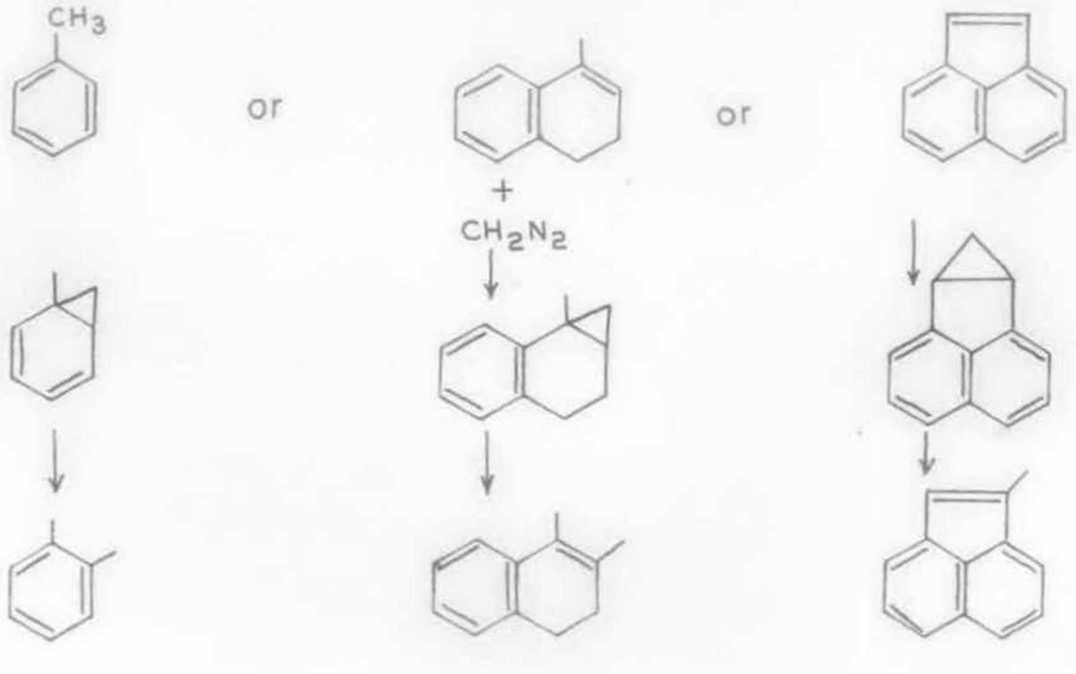
Experimental portion of this chapter has been described in this section.

Chapter-II:

This chapter deals with the decomposition of diazomethane with various copper salts.

Section-A:

This section deals with the aims and objects of this study when toluene, α-methyl 3,4 dihydro naphthalene and acenaphthglen were employed to be cycloproponated by means of diazomethane in presence of Cu and various copper salts. The aim being to derive an easy alkylation procedure or to prepare C-methyl derivative of these compounds by diazomethane.



Section-B:

This section contains the results and discussions of the previous reactions when solid product isolated other than C-methyl derivative of the reactants. This compound also prepared when ethereal solution of diazomethane alone was decomposed in presence of Cu or its salts.

This compound contained nitrogen but not Cu. It is highly alkaline in nature. When treated with KOH solution, it gave out a gas of ammonia like smell. It is not very stable in ordinary temperature. It melts at 112°C.

It showed following I.R. bands. (Fig 56)

Its molecular wt. by Beckmann depression of freezing point method was determined as also its nitrogen content to be 90.

It could not be hydrogenated. It does not contain any active olefinic double bond. No useful compound could be isolated when this oxygenated dimer was used in place of diazomethane itself in the various reactions indicated here.

Section-C:

Experimental portion of this chapter has been described in this section.