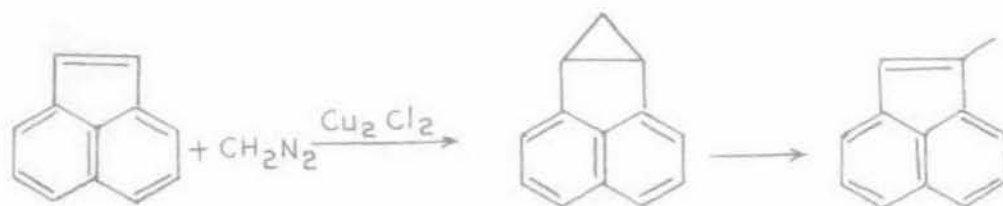
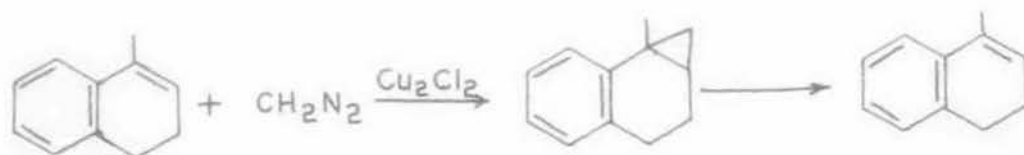


CHAPTER - II

Section-A : Aim and object of the decomposition of diazomethane with metal catalyst.

It is reported that diazomethane adds to double bonds forming cyclopropane derivative in presence of copper. Our aim was to prepare cyclopropane derivatives of methyl, 3,4^{dihydro} naphthalene and acenaphthene and thereby to see the insight of the state of CH_2 addition and its subsequent fate. Keto carbene addition to double bond in presence of copper catalyst was described as being effected via the singlet state. But methylene addition to double bond in absence of any catalyst was shown to be non stereo specific. So to find out any stereo specificity or not of methylene addition to double bond in presence of copper catalyst and to draw a relationship as to the state of methylene and that of the ketocarbene was our main objective. To prepare C-methyl derivative of α -methyl 3,4 dihydro naphthalene and acenaphthene was our main goal in this route.



Section-B : Results and Discussions.

Addition of diazomethane to some other olefins in presence of cuprous salts active copper powder was attempted. It is interesting to note in these connection that in the cases studied, addition to the olefins did not take place.

In a reaction of α -methyl 3,4-dihydro naphthalene, with diazomethane in presence of anhydrous cuprous chloride we isolated a solid product of m.p. 110-12^oC. In a similar reaction with acenaphthene we isolated the same solid product of m.p. 110-12^oC. Decomposition of an ethereal solution of diazomethane in presence of Cu₂Cl₂ or active copper furnished the same solid product of m.p. 110-12^oC. The same product also was isolated when the catalyst is anhydrous copper sulphate.

Some properties of this compound:

1. This compound decomposed slowly at room temperature and within 10 days it decomposed completely.
2. It contained nitrogen.
3. It was found to be highly basic in character.
4. When treated with KOH, it evolved NH₃ gas.
5. It could not be hydrogenated in presence palladised charcoal.
6. Heat and light decomposed the oxygenated dimer giving off nitrous fumes.
7. Pyrolysis of the compound in presence of reactive olefin did not give products that are obtained with diazomethane.

As it is decomposed very quickly, the elemental analysis of this compound could not be determined. Its molecular weights was determined by Beckmann freezing point depression method and molecular wt. was found to be 90.4.

Inspection of the I.R. spectra, it is seen that it contains a hydrogen bonded primary amine group. I.R. peak at 1780 cm^{-1} indicating that it may contain an amide function.

Inspection of the I.R. spectrum and molecular weight determination, it is suggested that the compound may be a polymer of diazomethane (a) or a formamide derivative (b). We could not give exact structure of this product still now.

Section-C: Experimental

(a) Decomposition of diazomethane in presence of copper sulphate.

In a one Lt. R.B. flask which was placed in a ice bath was taken 500 ml of ethereal solution of diazomethane prepared from 20 gms of nitrosomethylurea and which was dried on KOH pellets for 4 hours. In 500 mg anhydrous copper sulphate was added in one lot and the flask was fitted with calcium chloride guard tube. Immediate evolution of gas was observed. After two to three hours when ethereal solution became colourless the solvent was removed at room temperature using a water pump. When almost all the solvent was removed, the colourless solid was

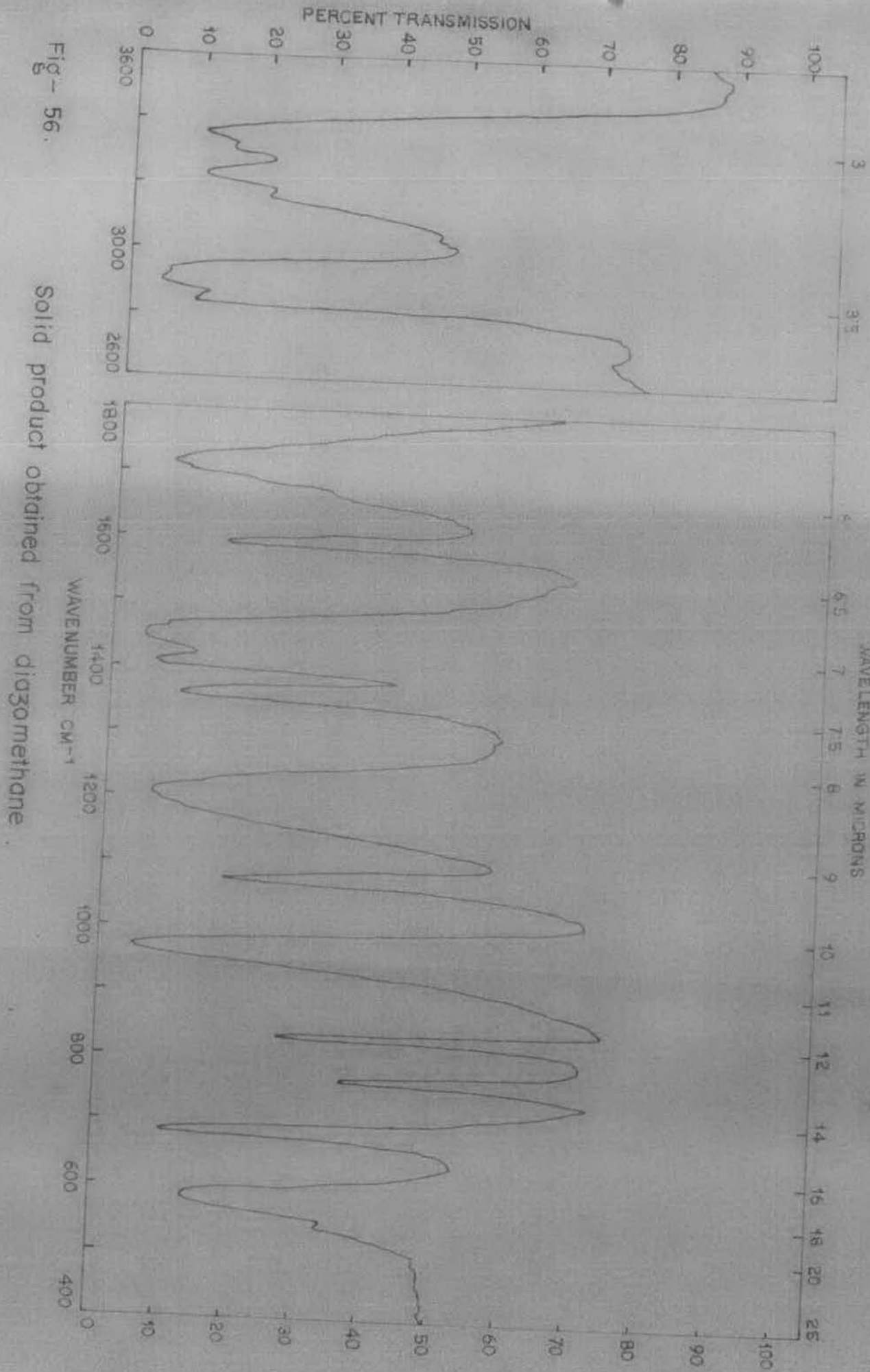


Fig- 56.

Solid product obtained from diazomethane

crystallised several times from dry benzene Yield-3.5 gm.
m.p. 112ⁱ.

(b) Molecular wt. determination by Beckmann freezing point depression method was found to be 90.4 .

1. Probable mole^{culab} formula could not be assigned.

2. Deoxygenation/Degassed Experiments.

(c) Analysis found N, 20%.

(d) I.R. Fig. 56.

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