

CHAPTER - III

DECOMPOSITION OF α -DIAZOTETRALONE

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A. Scope of the investigation

In this aspect of the investigation the principal aim was to prepare suitable α -diazoketones and to study its additions to various olefins via ketocarbene generation with or without catalyst. For this purpose various reactions of 2-diazo-1-tetralone and 3-diazocamphor were taken. Horner et al¹⁴³ first reported the preparation of these compounds from 1-tetralone and camphor respectively via the formation of oximinoketone and subsequent reaction with chloramine solution. We attempted their preparation via formylation¹⁴⁹ of ketones and subsequent deformylation via diazo transfer reaction¹⁵⁰⁻¹⁵². While 2-diazo-1-tetralone has obtained in good yield (70%), the formylation step of the camphor failed inspite of successive attempts. This 2-diazo-1-tetralone was taken to study the possible addition to different substituted olefin mainly. Our expectation was the formation of cyclopropane derivative of the ketocarbene but unfortunately in only one case the expected cyclopropane was formed. In all other experiments cyclopropane compound could not be isolated, instead the diazoketone decomposed and the olefin was recovered.

In oxidative decomposition diazocamphor, and diazoquinone have been proved to be very stable^{152a}.

B. U.V. Spectral Studies of 2-diazotetralone

It is a well known fact that α -diazoketone, undergo decomposition with the elimination of nitrogen upon heating with or without catalyst or under photolysis with or without sensitizers. Most α -diazoketones after losing nitrogen transform into keto-carbene which in turn react with a suitable olefin to produce a cyclopropane compound. It is reported⁷² that diazoc^fenaphthenone adds to olefin on thermal decomposition. Keeping this in view we prepared 2-diazo-1-tetralone via formylation of 1-tetralone and thereafter by diazo transfer reaction. The product of diazo transfer reaction was chromatographed for purification. We observed that the yellow bands of 2-diazo-1-tetralone in the chromatographic column of alumina changes very rapidly to dark red colour but the eluents remain yellow upto several days. Besides, the 2-diazo-1-tetralone crystals if kept open in the light turns dark red faster than the compound in the chromatography column.

Certainly the compound undergoes a chemical change accompanied by a change in the colour. Our interest was drawn to this rapid change in colour. We hoped that the

photosensitiveness of this compound will help us to study its decomposition rates. The U.V. absorption of the 2-diazo-1-tetralone was studied under different conditions. The various conditions are listed as follows:

1) Benzene solution of the compound kept in an open place to have light in absence of catalyst and heat.

2) Benzene solution of the compound was heated under reflux without applying catalyst. U.V. absorption were recorded, in this case, after an interval of a certain period.

3) Benzene solution of the compound was refluxed with freshly prepared copper powder catalyst. The absorption ~~W~~ has studied after a time interval.

4) Methanol solution kept in the light and U.V. absorption recorded at a time interval.

5) Decomposition product of step (3) above was dissolved in methanol and its U.V. spectra was recorded.

6) Carbon tetrachloride solution was kept in the light and its U.V. spectra were recorded at a time interval.

In all these experiments spec pure solvents and freshly crystallised 2-diazo-1-tetralone were used.

1) U.V. studies in Benzene solution in absence of catalyst and heat.

0.00198 gm of 2-diazo-1-tetralone was dissolved in

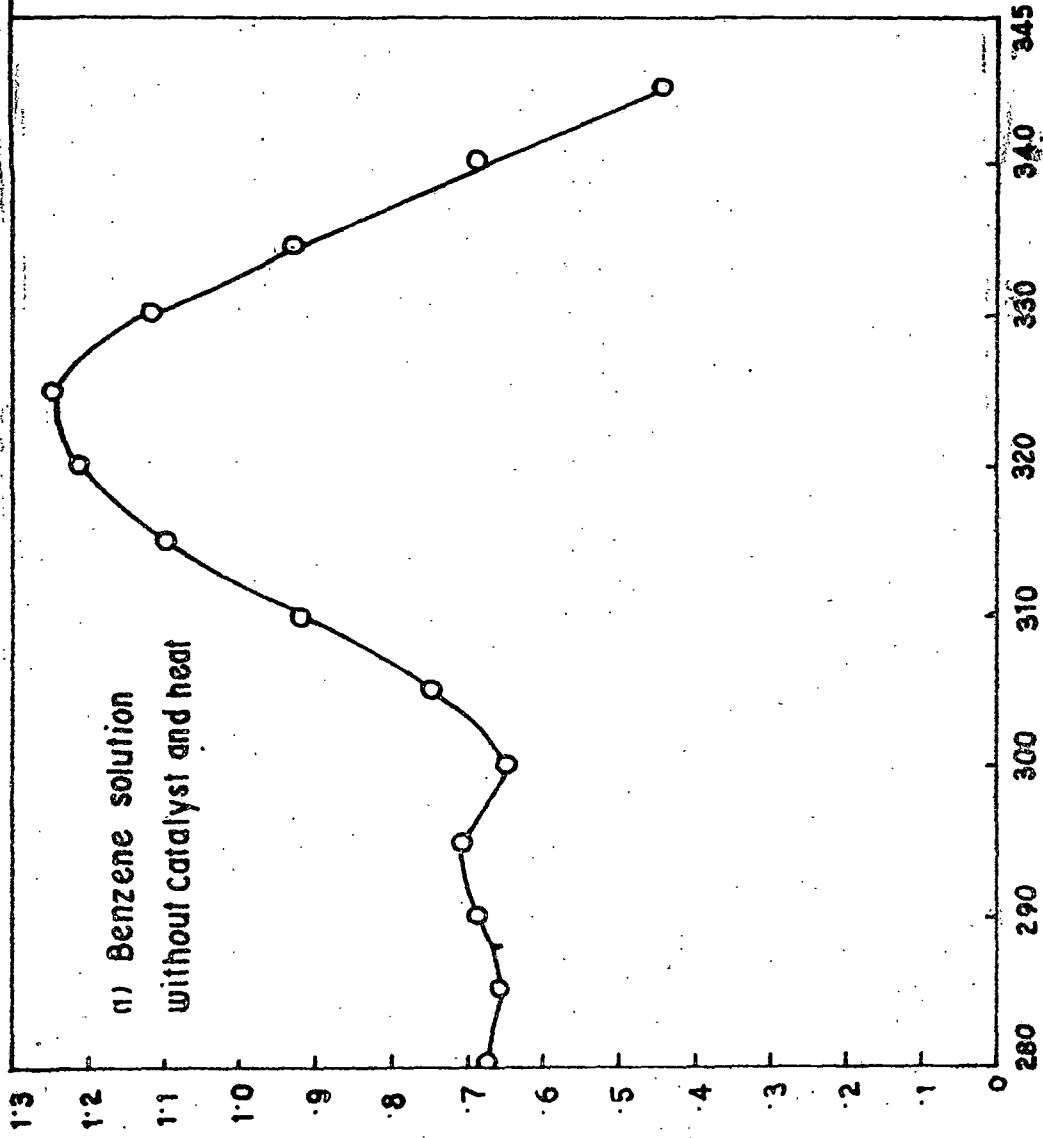


Fig 14. UV Spectrum in benzene solution

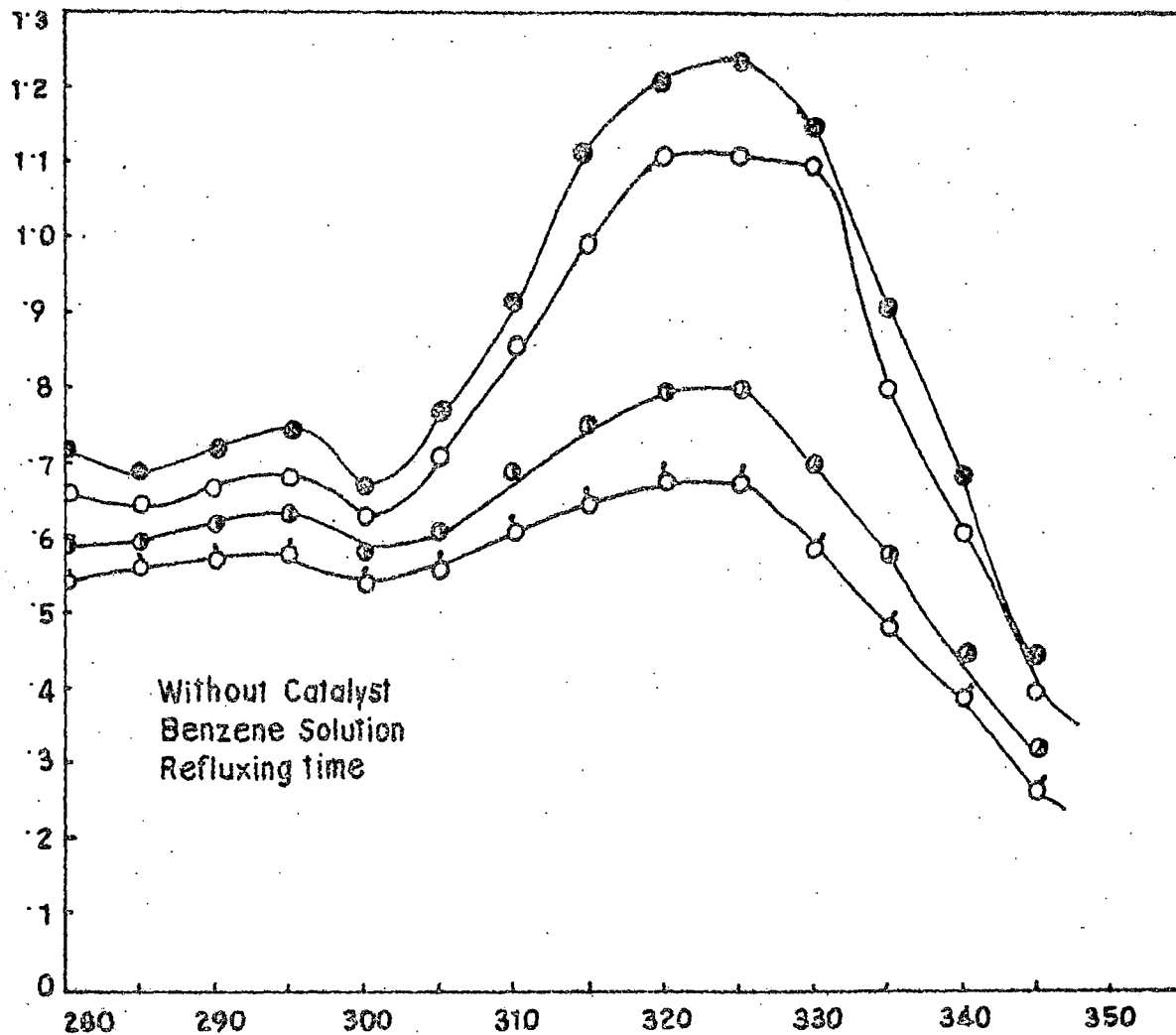


Fig 15. U-V spectrum ^{after} under refluxing condition

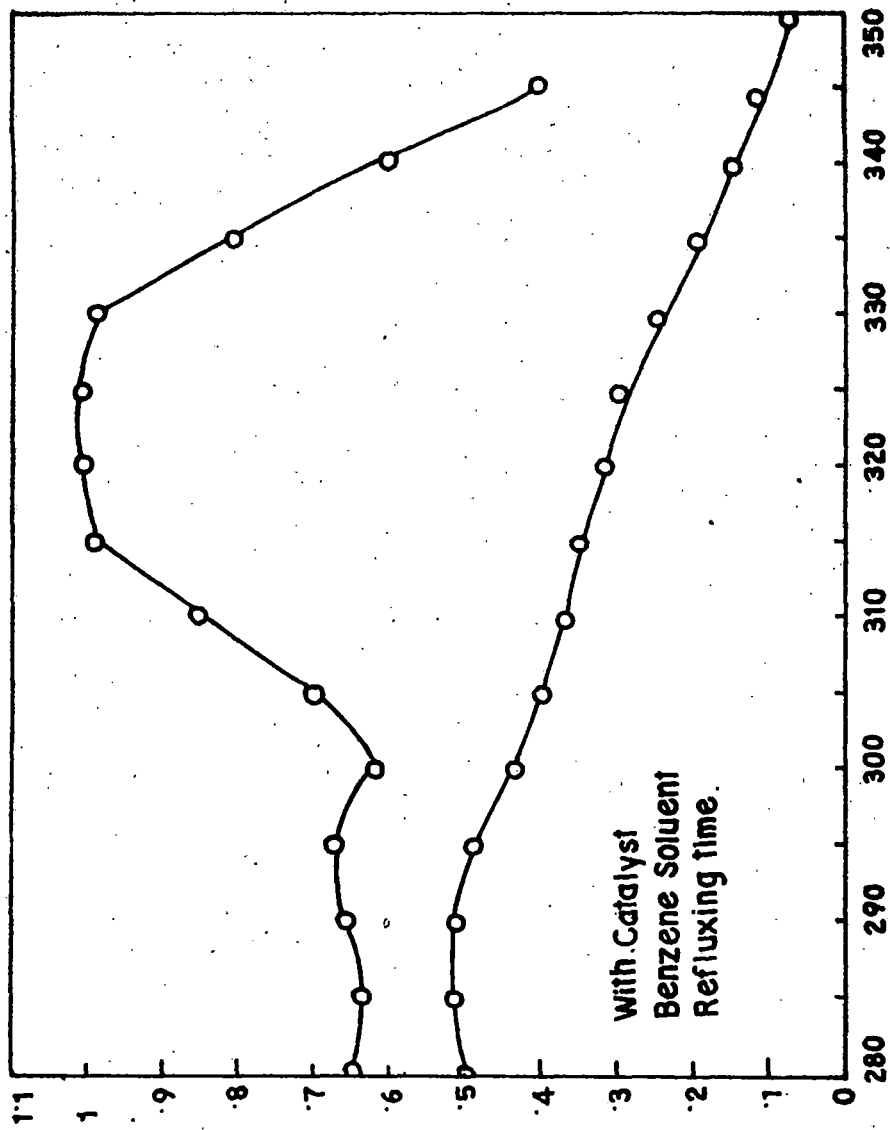


Fig 16. *u-v* Spectrum

10 ml of benzene and then 1 ml of this solution was diluted upto 10 ml. U.V. absorptions recorded at the start and then after every three hours interval. The process was repeated upto 48 hours. Virtually no deviation from the initial absorption was recorded. Fig. 14

2) Solution in benzene under refluxing condition.

0.01237 gm of 2-diazo-1-tetralone was taken in exact 50 ml of benzene and kept under reflux. After an interval of 3,6,16 & 20 hours the solution was cooled and 1 ml of this solution was drawn and diluted upto 10 ml and this solution was taken for U.V. spectra recording. The process was repeated upto 20 hours of reflux. Fig. 15

3) Solution in benzene under reflux with copper catalyst.

0.01161 gm of 2-diazo-1-tetralone was taken in exact 50 ml of benzene and 0.001 gm of copper powder was taken in and refluxed.

After the completion of 3 hours the solution was cooled and 1 ml of this solution was drawn by a pipette so carefully that no copper catalyst may come to the drawn solution. This solution was diluted to 10 ml and U.V. spectra recorded. The process was repeated after an interval of 6 hours. Fig. 16

4) Solution in methanol was kept in light.

0.00104 gm of 2-diazo-1-tetralone was dissolved

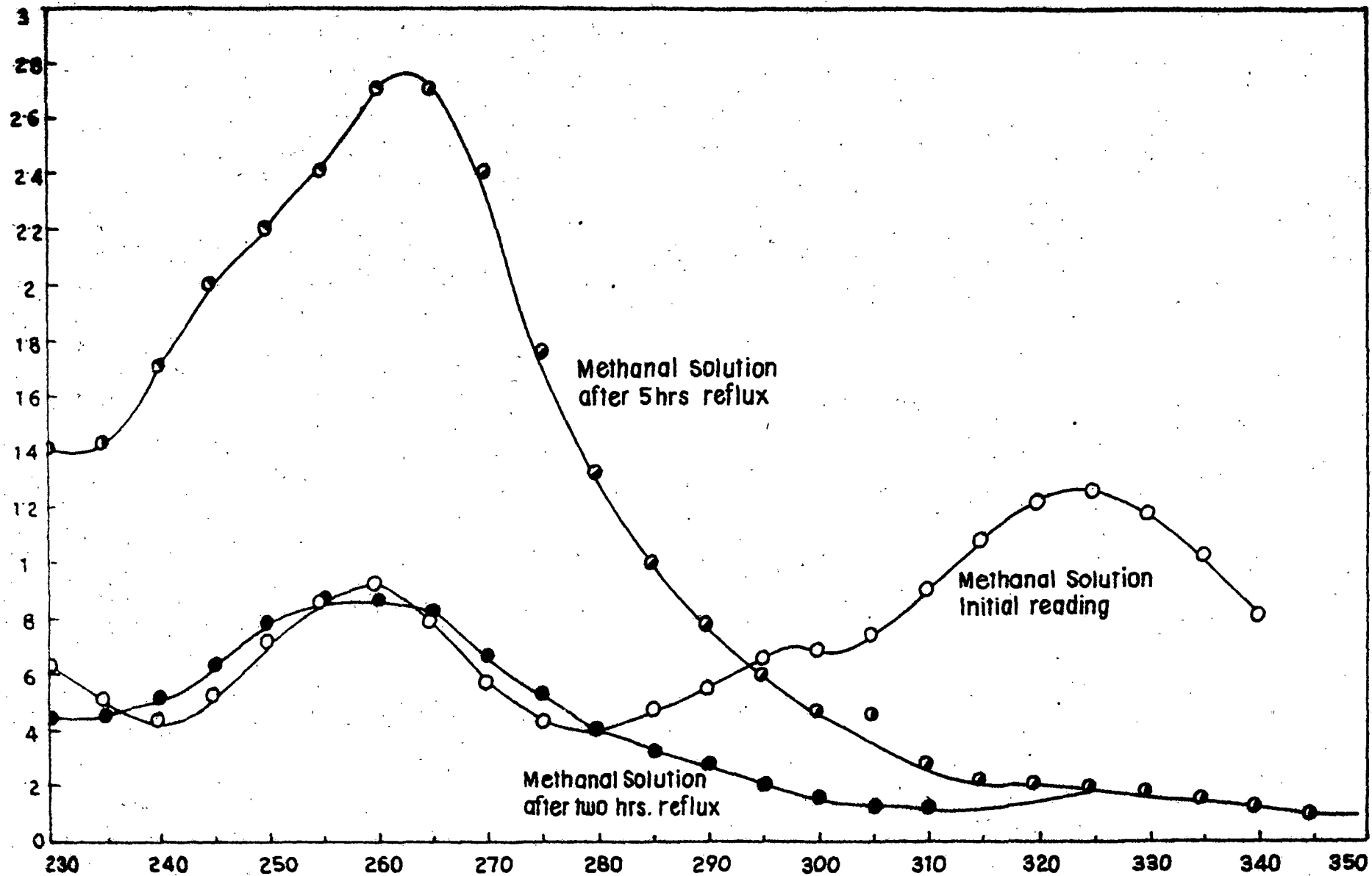


Fig 17. u-v Spectrum

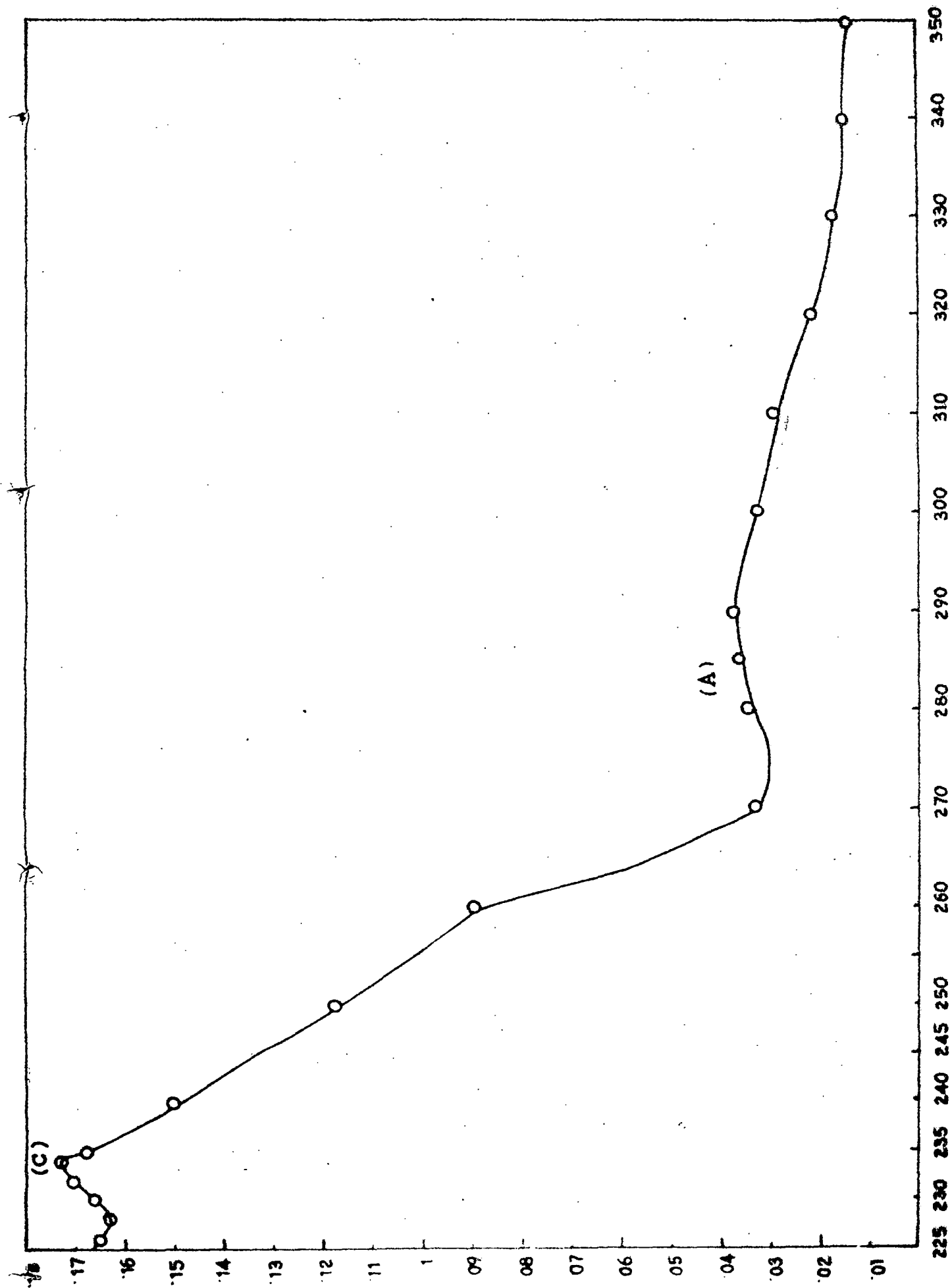


Fig 18. U-V Spectrum

in 10 ml of methanol and 1 ml of this solution was taken for U.V. absorption spectra, then repeated this experiment after an interval of 2 and 5 hours. Fig. 17

5) Residue of experiment (3) above in methanol solution.

After 6 hours reflux the solution was filtered to remove the catalyst and the solvent benzene was removed. The red residue was dissolved in 50 ml methanol and U.V. absorption of 1 ml of this solution diluted to 10 ml was recorded. Fig. 18

6) Absorption studies in carbon tetrachloride solution.

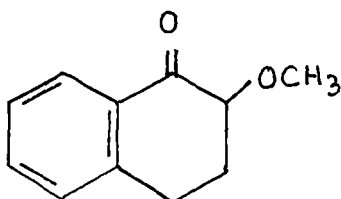
0.01440 g of 2-diazo-1-tetralone was taken in exact 50 ml of carbon tetrachloride. Then 1 ml of this solution was diluted upto 10 ml and this solution was taken for U.V. absorption spectra recording. ~~XXXXXXXXXX~~

C. Discussions and Conclusion

From figure 1 it appears that absorption peak for this diazoketone is at 325 nm. ~~XXXX~~ ~~XX~~. This value is unchanged on prolonged standing. Therefore, it is evident from this observation that no decomposition of the compound occurred and it is stable to light.

From figure II it appears that absorption peak for this diazoketone is at 325^{nm.} ~~XXXX~~ ~~XX~~ before heating was started. But after refluxing for three hours its ϵ is lowered and a gradual change of ϵ was observed till 20

react rapidly with methanol^{152b} forming keto ether. In this case also the following product formed initially.

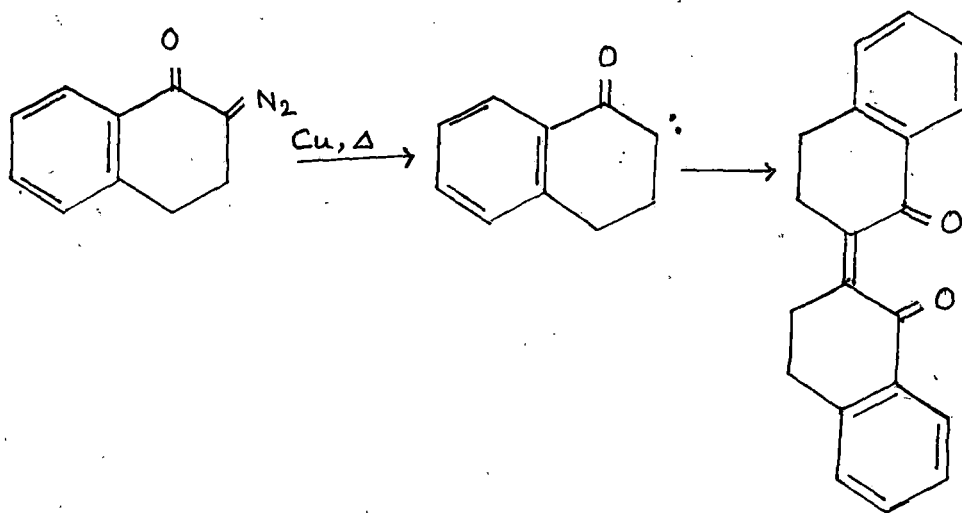


Absorption maxima of this diazo compound in CCl₄ solvent was found at 324 nm, but no appreciable change was observed when U.V. spectrum was recorded after a time interval. This finding also leads us to conclude that no decomposition occurred without heating.

From the foregoing it was clear that α -diazotetralone would be completely decomposed only when benzene solution of this compound was refluxed in presence of copper catalyst. Protic solvents will not give the products consistent with the keto carbene addition product with other substrate and non-polar solvents alone would not be highly satisfactory. α -Diazotetralone was treated with some olefin in presence or absence of catalyst but in only one case i.e. in the reaction between dimethyl fumarate and α -diazotetralone produced a keto carbene addition product. Other olefins which were subjected for reaction with diazotetralone under

the same condition did not give any such addition product whereas these olefins were capable of giving addition products with benzoyl carbene.

Inertness of the diazotetralone towards various olefins might be due to the peculiar nature of the decomposition of the diazotetralone. The keto carbene addition product of dimethyl fumarate may be explained by the fact that the role of substrate has a definite positive influence to favour the ketocarbene addition compound formation besides the catalytic activity of active copper powder. Formation of keto carbene was not observed when diazoacenaphthenone was refluxed with catalyst in absence of substrate whereas addition products were obtained when refluxed with dimethyl fumarate and other olefins. Thus α -diazotetralone shows a behaviour somewhat analogous to that of α -diazooacenaphthenone. Thermal decomposition product of diazotetralone alone in presence of copper catalyst was isolated, but it was not fully characterised because it might be a dimer of keto carbene thus formed.



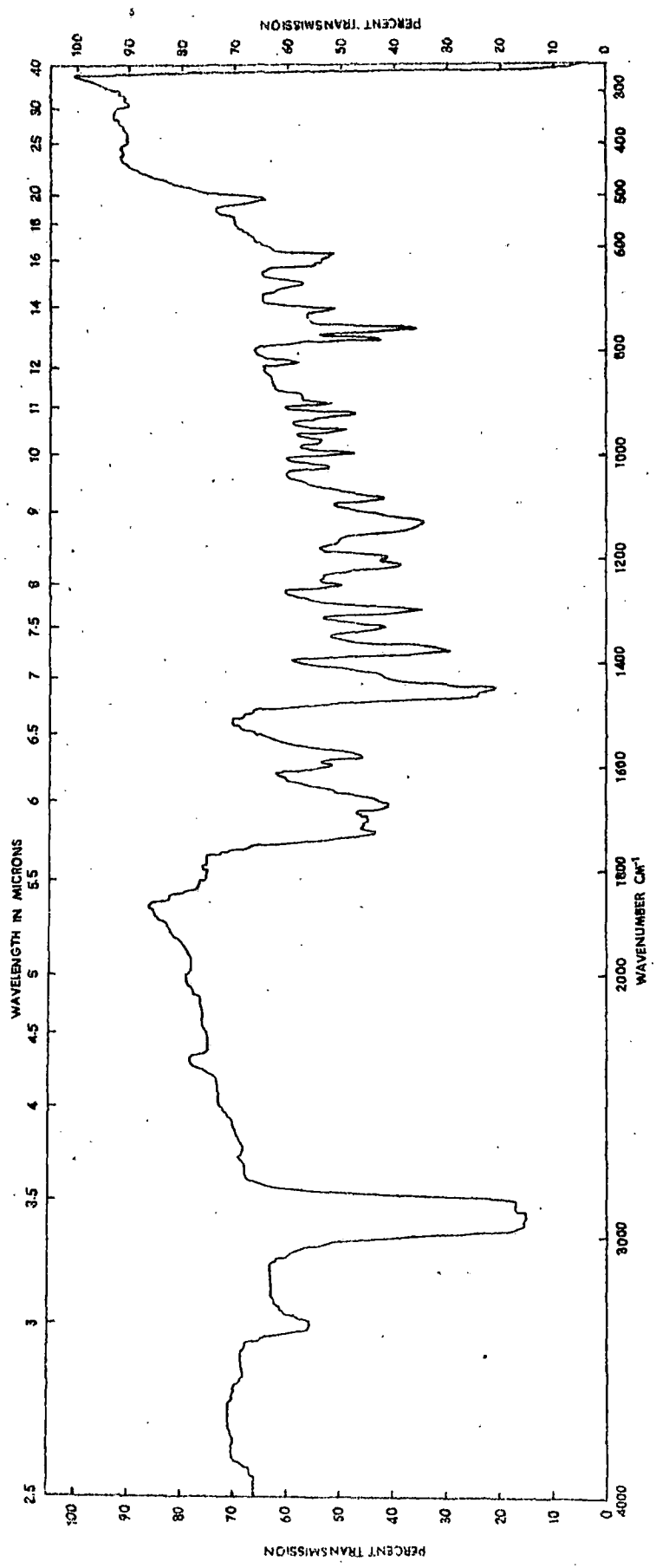
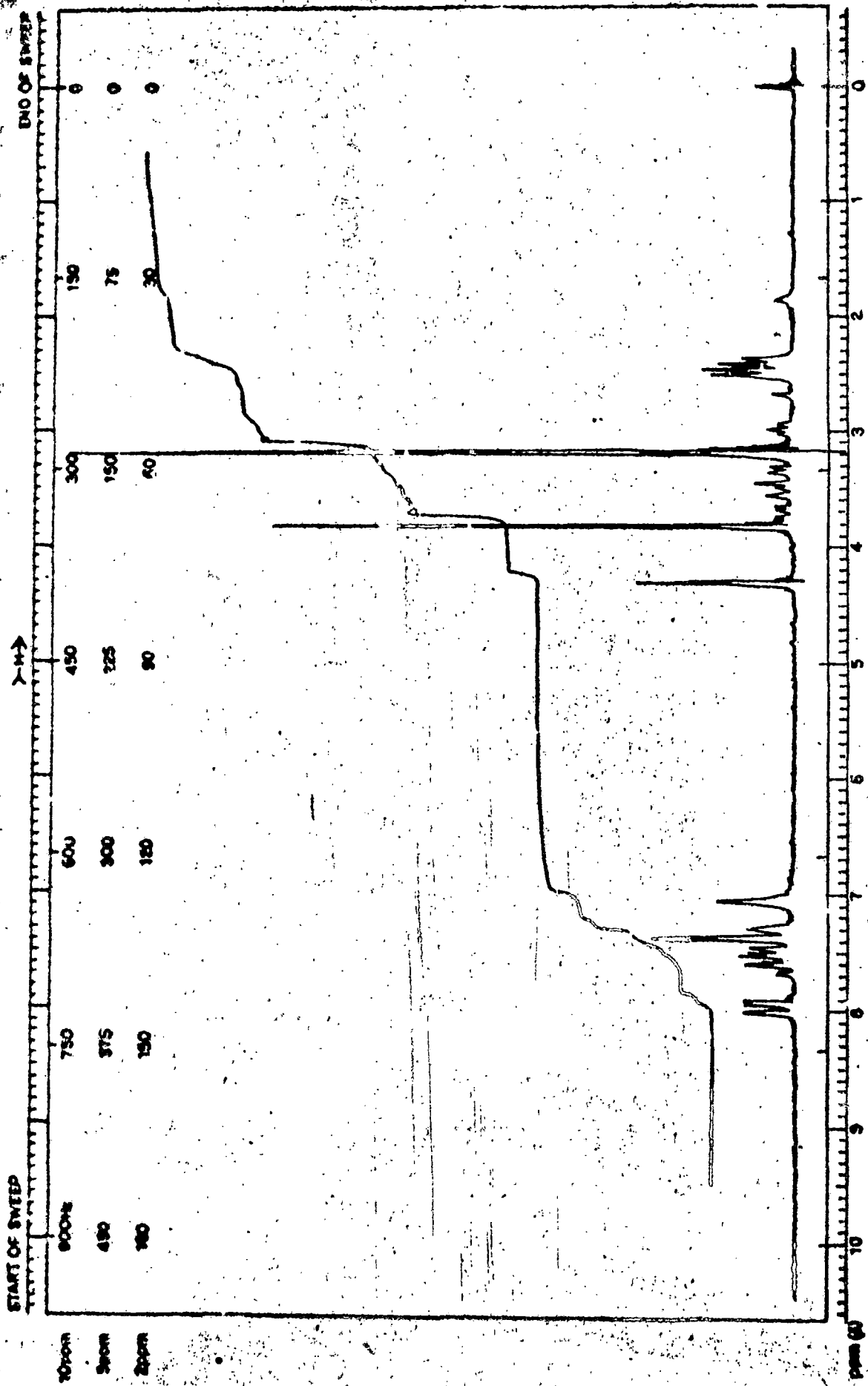


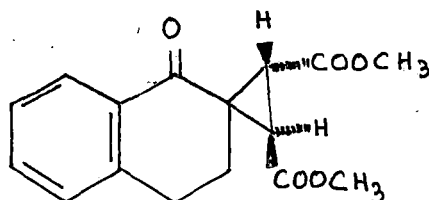
Fig 19 I.R. spectrum of trans-2,3'-dimethoxy carbonyl spiro [tetrahydro-1(2H) naphthalenone - 2,1'-cyclopropane] (IX)



NMR spectrum of IX

(IX)
Reaction product of diazotetralone with dimethyl fumarate was fully characterised by analysis, I.R., N.M.R. and mass spectral studies.

IR (Fig. 19) peaks at 1730 cm^{-1} , 1680 cm^{-1} and 1020 cm^{-1} indicate that the compound contains ester, carbonyl function and a cyclopropane ring. On this ground, structure of the compound may be written as



IX

NMR of this compound (Fig. 20) in CDCl_3 shows the signals at δ 7.4 (aromatic proton), δ 3.8 (carbomethoxy proton), δ 3.2 (^{trans} carbomethoxy proton), δ 2.15 to δ 2.6 (quartet) (aliphatic proton), δ 1.7 (cyclopropane proton). These signals are consistent with the structure given above. There is no signal for the olefinic proton which shows olefin is totally absent.

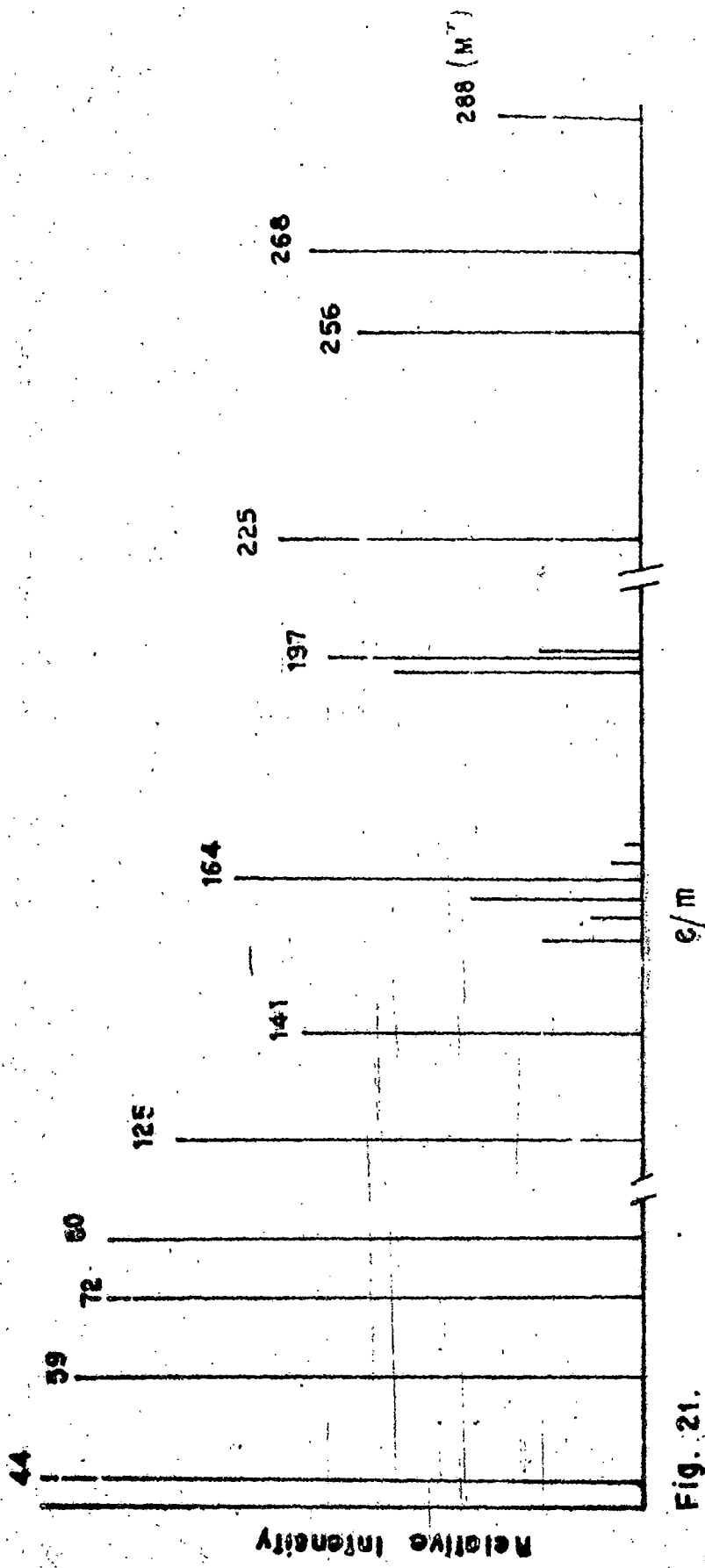
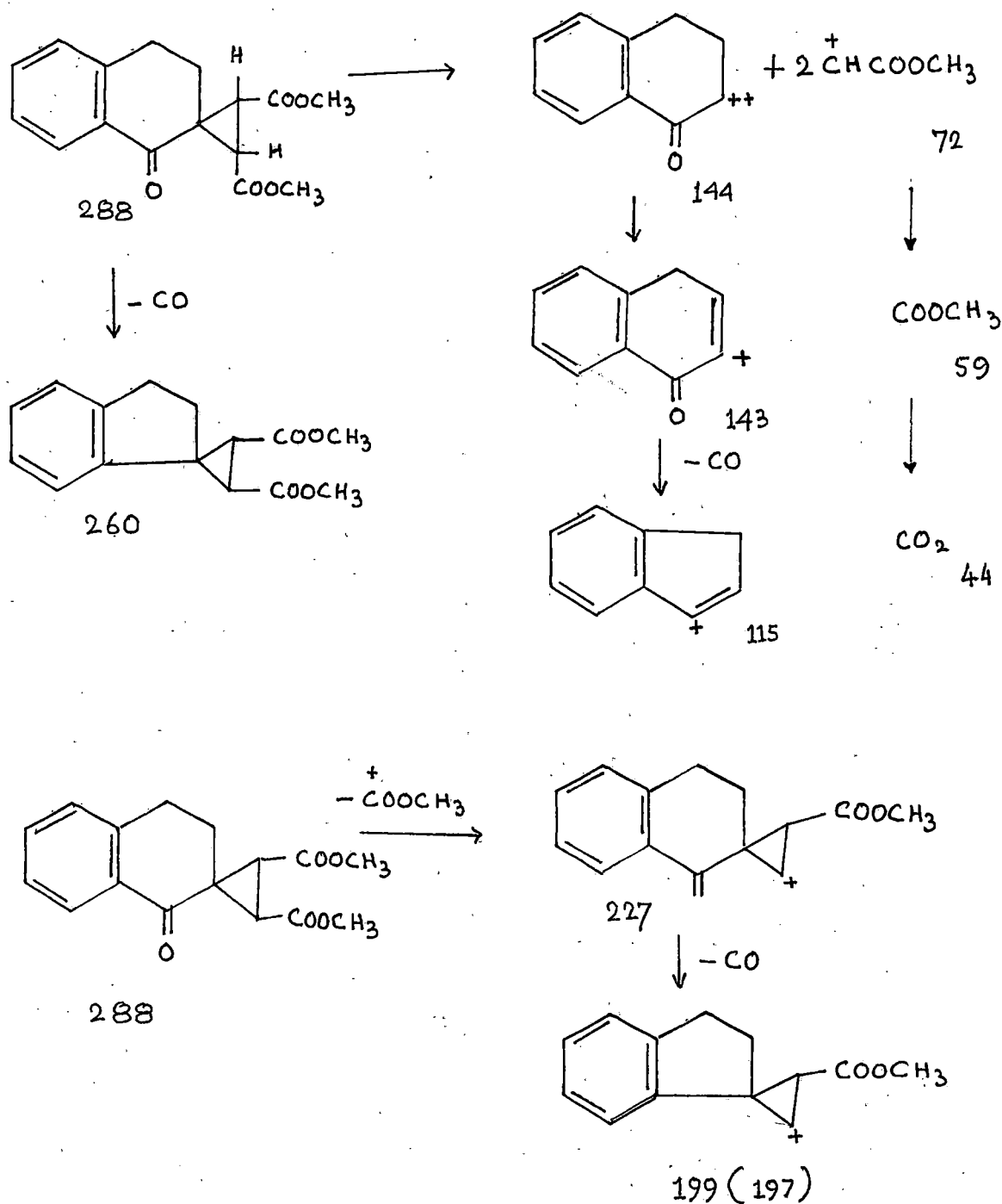


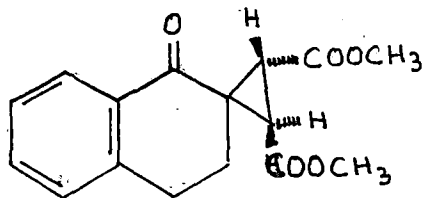
Fig. 21.

Mass spectrum of IX

Mass spectrum (Fig. 21) shows the peaks at 288 (M^+), 268, 256, 225, 197, 164, 141, 125, 80, 72, 59, 44. These peaks may be explained assuming the fragmentation in the following way.



Considering all the above evidences the structure of the keto carbene addition product of diazotetralone and dimethyl fumarate was assigned in the following way.



D. Experimental

1. α -Tetralone¹⁵³

A 3 litre three-necked flask was fitted with a mechanical stirrer, an efficient condenser capped by a drying tube filled with calcium chloride, and a wide-bore rubber tube leading to a one litre conical flask. One litre dry, thiophene free benzene and 104 gm (1.21 mole) of γ -butyrolactone were placed in the 3-litre flask. 600 gm (4.5 mole) reagent grade anhydrous aluminium chloride was placed in the conical flask and was added to the stirred reaction mixture during a period of 2 hours. The mixture became dark brown, refluxed gently, and evolved hydrochloric acid gas. After addition of all the catalyst, the mixture was heated on a steam bath with continued stirring of 16

hours. It was then cooled to room temperature and poured onto 3 kg of crushed ice drenched with 500 ml of conc. hydrochloric acid. The lower aqueous layer was separated and extracted with about 500 ml of toluene. The brown, organic upper layer and toluene extract were combined, washed successively with water, 20% potassium hydroxide and water, and distilled under reduced pressure to remove benzene toluene and trace of water. Distillation of the residue in a claisen flask yield 140 gm of α -tetralone. There was a residue consisting of 130 gm of red-purple viscous oil, b.p. 140° - 45° /3 min.

2. p-Toluene sulphonylazide¹⁵⁴

A solution of 12 gm of sodium azide in 35 ml of water was placed in 500 ml round bottled flask and diluted with 70 ml of 90% aqueous ethanol. To this solution was added with stirring a warm (45°C) solution of 32 gm of p-toluene sulphonyl chloride in 170 ml of 99% ethanol. During this addition sodium chloride separated and the reaction mixture turned into brown colour. The reaction mixture was stirred at room temperature for 2.5 hrs. After the reaction was over most of the solvent was removed by distillation at 35°C (15 mm). The residue was mixed with 500 ml of water in a separatory funnel, and the oily p-toluene sulphonyl azide was separated. The oily product was washed with two 20 ml portions of water and dried over anhydrous sodium

sulphate. Filtration with suction gave 24 gm of pure colourless p-toluene sulphonyl chloride, solidifies on standing in the refrigerator.

3. 2-Hydroxy methylene tetralone¹⁴⁹

A mixture of 4.6 g of molecular sodium metal, 500 ml of dry ether, 29.2 g of redistilled α -tetralone and 22.0 g of ethyl formate was introduced successively into a 1 litre-3-necked flask equipped with a mechanical stirrer and a calcium chloride guard tube. The reaction was initiated by the addition of 1.3 ml of ethyl alcohol the flask placed in a cold water bath. Stirring continued for 6 hrs. After standing overnight, 5 ml of ethyl alcohol was added and the mixture was stirred for an additional hour. After the addition of 50 ml of water, the mixture was taken in one litre separatory funnel. The ether layer was washed with 15 ml of water and the combined aqueous extract washed with 25 ml of ether. The aqueous layer was acidified with 33 ml of 6N hydrochloric acid, and the mixture was extracted twice with 100 ml of ether. The ether solution was washed with 6 ml saturated sodium chloride solution and then dried over anhydrous sodium sulphate. Sodium sulphate was filtered and the solvent was removed and the residue was distilled at 120-125° C/4 mm. Yield 15g.

4. 2-Diazotetralone¹⁵⁵

In a 500 ml 3-necked flask were mixed 8.7 g of 2-hydroxymethylene tetralone, dichloromethane (40 cc) and triethylamine (10.6 g). The flask was cooled in an ice salt bath at -15°C and p-toluene sulphonyl azide (9.8 g) was added with vigorous mechanical stirring over a period of 1 hr. at such a rate that the temperature of the reaction mixture could not rise above -5°C . Stirring was continued for an additional two hours as the cooling bath melts. A solution of potassium hydroxide (3.08g) in water (4 cc) was added and the mixture was stirred for 15 minutes at room temperature. The resulting emulsion was placed in 500 ml separatory funnel, the dichloromethane layer was separated after standing and the aqueous layer was washed with two 20 ml portions of dichloromethane. The combined dichloromethane solution was washed with a solution of potassium hydroxide solution (0.1 gm in 5 ml water) and then with 10 ml of water and dried over anhydrous sodium sulphate. The solvent was removed on a rotary evaporator at 35°C . The pink-brown residue chromatographed through an alumina column. Orange-yellow crystals of 2-diazotetralone were obtained from the petroleum ether fraction which was recrystallised from 10% benzene and 90% petroleum ether m.p. 52°C . Yield 7.0g.

5. Dimethyl maleate¹⁵⁶

10 gm of maleic acid and excess dry methanol (250 ml) and 1 ml of conc. sulphuric acid was refluxed for 10 hours. Then the solvent was removed under reduced pressure and the liquid residue was extracted with solvent ether and ether solution was taken in a separatory funnel washed successively with 5% sodium bicarbonate solution and water till neutral. Anhydrous sodium sulphate was added to the ether solution and filtered to separate the solution. Solvent was removed and the residual liquid was distilled at the pump. Boiling point 202°C.

6. Dimethyl fumarate¹⁵⁷

10 gm of fumaric acid and excess dry methanol (250 ml) and 1 ml conc. sulphuric acid was refluxed for 10 hours and worked up in the same manner as above. After removal of the solvent ether a solid was obtained, recrystallised from methanol, colourless plates of m.p. 103°C was obtained. Yield 6.5 g.

7. Methyl cinnamate

15 gm cinnamic acid dry methanol (250 ml) and 1 ml conc. sulphuric acid was refluxed for 6 hours and the reaction mixture was worked as in (15). After solvent removal a liquid residue was obtained which on cooling solidifies.

Recrystallisation from methanol colourless needles. M.P. 37° of methyl cinnamate was obtained.

8. Methyl crotonate

50 g of pure crotonic acid, 75 cc dry methanol and 2.7 cc concentrated sulphuric acid were placed in a 250 ml dry round bottomed flask and refluxed for 12 hours. After completion of 12 hours water was added to separate the ester and extracted with ether, washed with dilute sodium carbonate solution until effervescence ceases, dried over anhydrous sodium sulphate and ether was evaporated off. Residue was distilled at $118-120^{\circ}$, yield 4g.

9. Reaction of 2-diazotetralone with dimethyl fumarate. /

850 mg of 2-diazotetralone and 1.5 g of dimethyl fumarate in 50 ml dry benzene was refluxed for 6 hours. Solvent was removed under vacuum when semicrystalline residue was left. This residue was triturated with petroleum ether ($40^{\circ}-60^{\circ}$), leaving the immiscible red dimeric part in the flask. The petroleum ether solution was heated to remove solvent when colourless crystals of the product obtained. This was recrystallised from methanol twice when colourless shining crystals of the product was obtained. M.P. 161° yield 400 mg.

Analysis	Calc. C, 66.66%	H, 5.55%
	Found C, 60.64%	H, 5.13%

10. Reactions of 2-diazotetralone with cyclohexene, methyl cinnamate, o-methoxy methyl cinnamate, trans-phenylmethyl cinnamate, methyl crotonate and dimethyl maleate were carried out as in (9) above but as the products could not be characterised fully their experimental details have not been furnished.