PHOTOCHEMICAL AND PHOTOPHYSICAL STUDIES ON ISATIN

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TABLE OF CONTENTS

LIST OF FIGURES

Photochemical and Photophysical Studies on Isatin

ABSTRACT

The fading rate of isatin in different solvents is investigated. The rate is in accordance with the hydrogen - atom donation capacities of the solvents. As the polarity of the solvent is increased the charge transfer character of the longest wavelength transition becomes dominat which prohobits photoreduction. This was confirmed by the red shift of the wavelength of maximum absorption with increase in solvent polarity and comparative fading rate of the derivatives of isatin (N - methyl isatin and N - acetyl isatin).

Molecular oxygen was found to quench the photoreduction. Fluorescence spectrum at different oxygen concentration has been investigated in an attempt to trace the spin state from which the reaction starts.

Two photoproducts were separated, the major product (over 95%) was characterized to be a pinacol and the second is the product of insertion of a single oxygen to isatin molecule.

A C K N O W L E D G E M E N T S

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I. INTRODUCTION

1. Scope of the work

A study on the photodecomposition of indigo[1] conducted in this department resulted in the isolation of isatin as one of the products. It was not clear, however, if isatin underwent further photodecomposition to give any of the other products. Survey of the literature indicated that the photochemistry was not adequately studied and the few scanty reports were not conducted in the manner reported for indigo[1]. This project was, therefore, undertaken to carry photochemical and photophysical studies on isatin.

In this study, an attempt is made to determine the type of photochemical excitation process. This is done by investigating the effects of different solvents and monitoring the resulting shifts induced by addition of acid and comparison of spectra with those of hydrocarbons of similar structure.

Flourescence and phosphorescence measurements were also carried out in an attempt to trace the spin state from which photochemical reactions of isatin occur. The quantum yield of the photoreaction and the quenching effect of molecular oxygen on the reaction quantum yield and flourescence have also been studied.

Finally structures are proposed for the two photoproducts on the basis of spectroscopic and chemical data.

2. Historical

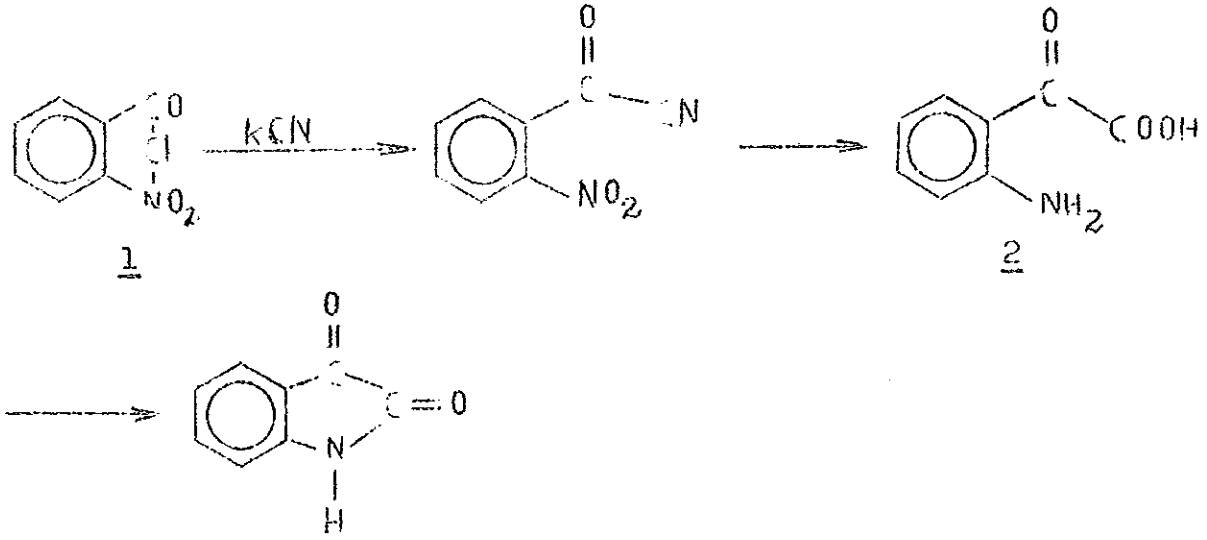
In the course of studies on the action of various oxidizing agents on indigo Erdmann[2-4] and Laurent[5-7] in 1841 independently discovered an oxidation product which had the formula $C_8H_5NO_2$ and to which the name isatin was given. The preparation of the compound was best effected by the action of nitric acid or a mixture of nitric acid and chromic acid on indigo.

In 1845 Hofmann[9] found that heating isatin with strong alkali gave aniline and that similar treatment of chloro-isatin yielded chloroaniline. Subsequently Hoffman[10] in 1860 showed that treatment of isatin with nitrous acid gave 5-nitrosalicyclic acid.

Isatin was found to dissolve in alkali to give the salt of an acid, isatic (isatinic) acid Kekule[11] in 1869 offered the suggestion that isatic acid was o-amino-benzoyl formic acid (2) and that isatin was its lactam, and proposed that isatin might be synthesized from o-aminophenylacetic acid.

The synthesis of isatin (3) from o-nitro benzoyl chloride (1) by Claisen and Shadwell[14] in 1879 furnished definite

confirmation of the structure suggested by Kekule. These workers suggested that isatin represents the first recognized case of a tautomeric substance.



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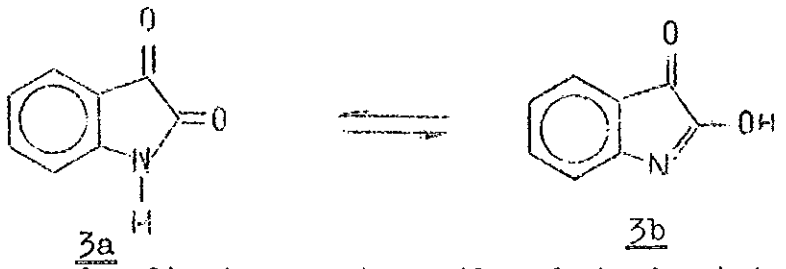
In 1882 Bayer [12,13] conducted further experiments on isatin and demonstrated that it reacts in both the lactam (3a) or lactim (3b) form.



3a 3b

The first report on the photochemistry of isatin appears in 1902 when Ciacian and Silber[16] reported an unidentified compound of empirical formula $C_8H_7O_2N$ by exposure of isatin in ether to sunlight.

In variance to the work of Ciacian and Silber in 1949 Emanuale Oliversi[15] exposed ethanolic and ethereal solutions of isatin to sunlight as well as UV-radiation and reported that no photoproducts were formed.

In 1967 Nobre Sugiyamo[17] studied the chemiluminescence of isatin in different reaction systems.

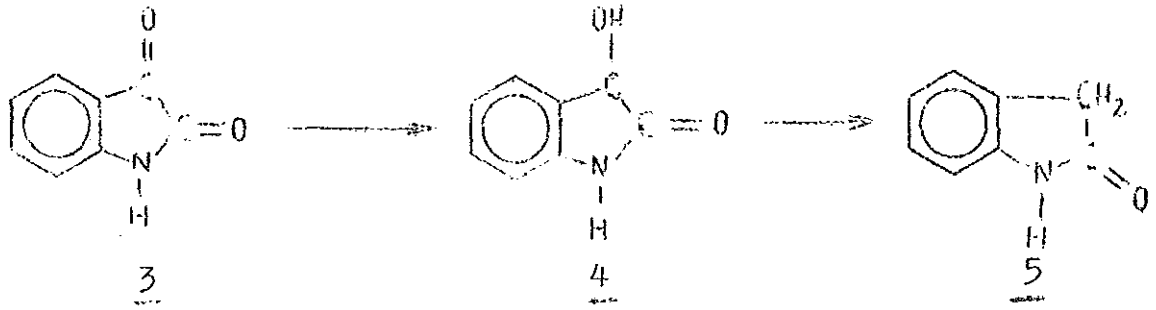
The above mentioned three reports constitute the current knowledge on the photochemistry of isatin prior to the work reported in this thesis.

II. PHYSICAL, SPECTROSCOPIC AND CHEMICAL PROPERTIES OF ISATIN

Isatin crystalizes from water, alcohol, or acetic acid in the form of red needles melting at 200-201°C. It is soluble in hot water, alcohol, acetic acid, concentrated sulfuric acid and benzene but sparingly soluble in ether. It dissolves in sodium or potassium hydroxide solution, forming the sodium or potassium salt of isatin[18]. Heating the solution of sodium or potassium salt results in the ring opening with the formation of the salt of isatinic acid. When the solution is acidified ring closure results and isatin precipitates.

Eventhough isatin has two carbonyl groups, the one at C-2 is part of an amide structure and thus the molecule does not behave like a diketone. The carbonyl group C-3 undergoes the usual reactions. Isatin reacts with sodium bisulphite and gives a phenylhydrazone with phenyl hydrazine. The reactivity of the C-3 carbonyl group is also reflected in the reduction of isatin (3) with Zn/HCl to give dioxindole (4) or oxidole (5) according to the strength of the acid used[19].

The existence of tautomers of isatin has been demonstrated by alkylation experiments[19]. Thus the nitrogen can be easily acetylated, benzoylated or methylated. If, however, the red siliver salt of isatin is treated with



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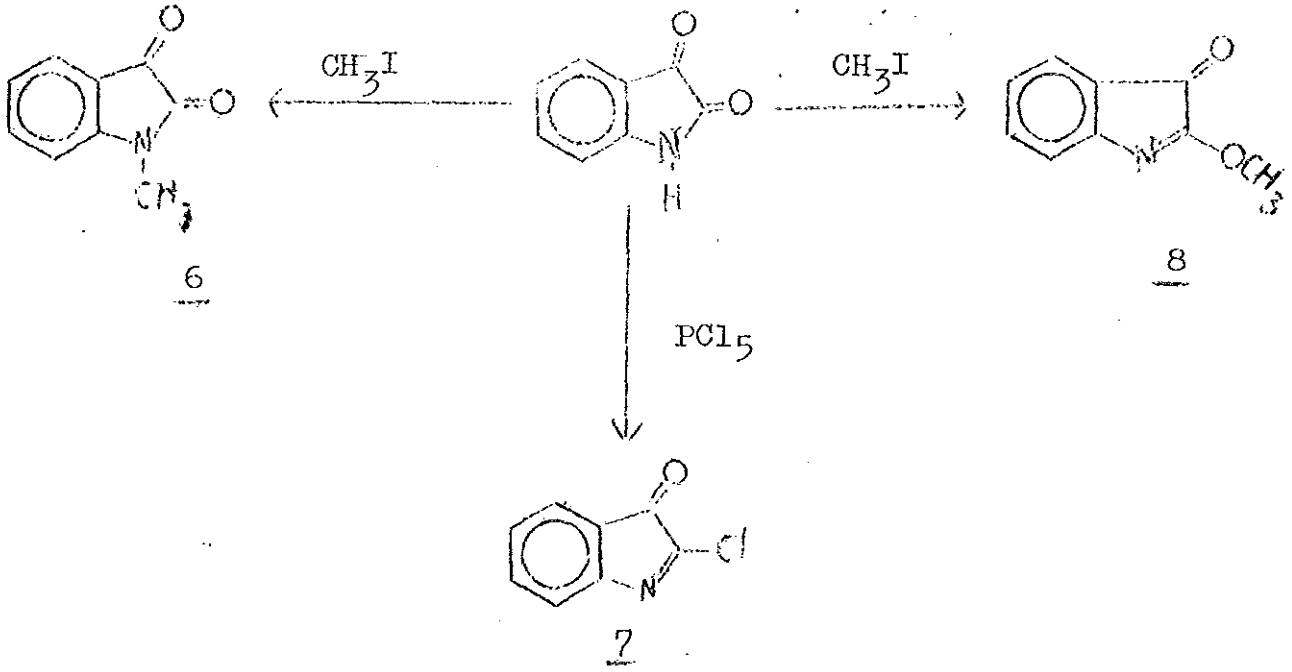
CH_3I, C-methyl isatin (8) is obtained. The lactim structure is also shown by warming a benzene solution of isatin with PCl_5 when isatin chloride (7) is obtained[19].



6 8 7

The greater similarity of the visible absorption of isatin to its N-methyl derivative than its O-methyl ether was used as an evidence by Hartely and Dobbie[20] to conclude that the lactim structure (3b) was preferred.

However, this claim was questioned by other workers[21-23] who indicated that data from this spectral region could not be interpreted unambigously.

Fig.(1) showes the various bond distance of isatin obtained from X-ray data[24]. The normal value for C = O bond length is 1.21Å. The C-3-O bond distance in isatin is shorter by 0.02Å while the C-2-O distance is 1.21Å. This observation can be rationalized by assuming the C-3-O bond some 15-20%. The shorter length of C-3-O bond than that of a normal C=O must mean that this bond has a greater double bond character.

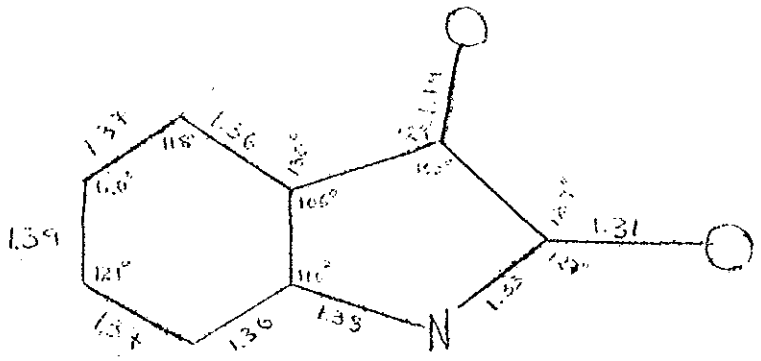


Fig (1) Bond angle and Bond length of isatin

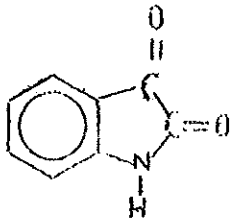
It is obvious, therefore, that those resonance forms involving single-bond character for either or both C-2-O and C-3-O contribute very little.

Cowley[23] suggested that the high dipole moment of isatin in dioxane favours the lactam formulation. Cox, Goodivers and Wagstaff[24] showed from an X-ray study of

isatin crystals that the molecules are arranged in parallel layers with the N and O atoms of one molecule only 2.8Å distance from O and N atoms respectively of the adjacent molecules in the same layer. The situation was strongly indicative of intermolecular hydrogen bonding, the presence of which is in accord with the solubility characteristics of isatin in various solvents. For the relevant parts of two adjacent molecules, structures (12) and (13) should contribute to the resonance hybrid structures, (14) not only strengthens the intramolecular bonding, but also increases the lactam character of the individual molecules.

Further X-ray investigation by Goldschmidt and Llewellyn[24] led to a revision of the interamolecular N-O distance to 2.93Å and to the claim that the bonded molecules were not coplanar. The molecule mapping was stated to be consistent with contributions of 62%, 10% and 10% fror(12)(13) and (14) respectively, and a further 10% arising from two structures in which the oxygen atom of the carbonyl group carries a negative charge. The total lactam contribution was estimated to be 85%.

Mangni[25] studied the absorption bands of isatin and its derivatives and it was found that isatin and its derivatives show three absorption bands in ethanol at 242-261 mμ log 4.20; which is attributed to the



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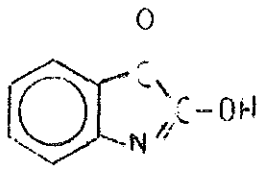

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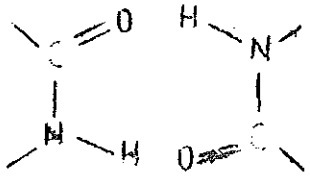

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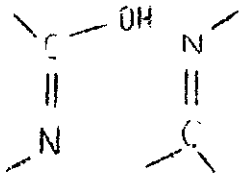

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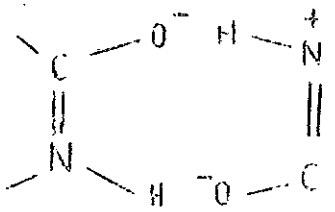

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excitation of the benzene ring; at 298-320 mμ, log 3.5 - 3.7 due to -C = O; and above 400 mμ due to -NH-CO.

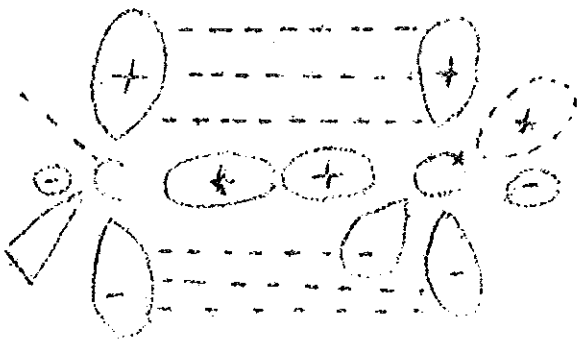
Sadwick[26] (1959) observed a shift towards longer wavelength in alkali solution of isatin as compared to neutral solution which was attributed to the formation of the anion.

III. PHOTOCHEMISTRY OF KETONES

Photochemical reactions of carbonyl compounds account for a very large proportion of all known photochemical reactions. This is due to the fact that the carbonyl group can be selectively excited and it is highly reactive. Its reactivities are different in the ground and in the excited states.

1. Types of transition and their assignments

The MO description of ketones assigns a pair of nonbonding electrons to the carbonyl oxygen which are directed in the plane of the molecule but perpendicular to C=O bond axis.



The lowest energy transitions are $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ in which either an n- or a π-electron is transferred to an antibonding orbital. For simple aliphatic ketones

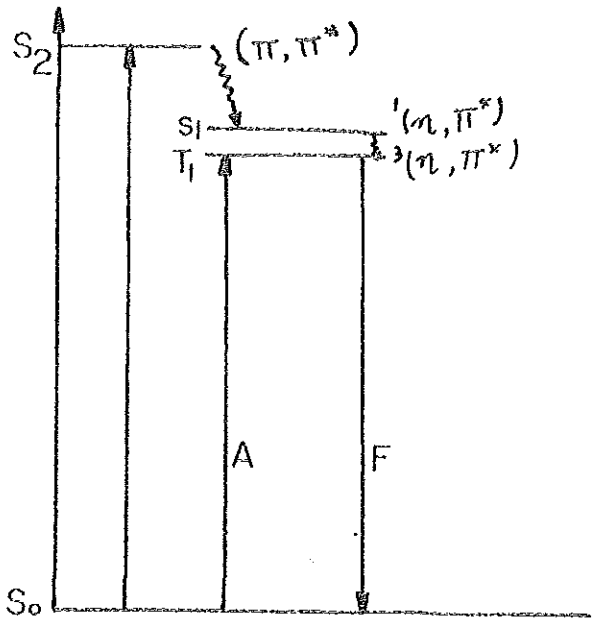
the lowest singlet state is S_1 (n,π^*) and the corresponding triplet $T_1(n, \pi^*)$. In aromatic ketones singlet may still be $S_1(n,\pi^*)$ but the lowering of (π, π^*) state may bring the $T(\pi, \pi^*)$ in proximity of $T(n, \pi^*)$ or even below the later. Therefore, in a substituted aromatic ketone the nature of the substituents decides the lowest triplet state[29].

In plotting the energy level diagram for transition in ketones three representative cases can be identified. Type 1, which is a characteristic of simple aliphatic ketones, the (n,π^*) transition is the one of lowest energy.

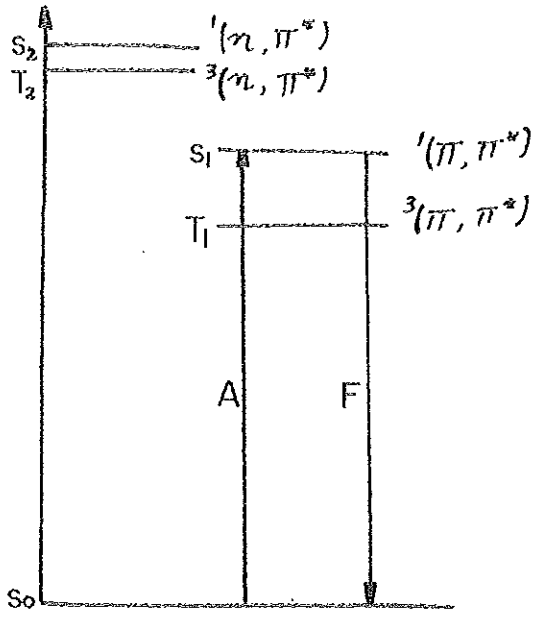
Type II is the case where the (π,π^*) transition is lowered either by conjugation or by substituents. Type III represents an intermediate between these two extremes.

The third type of transition, known as charge transfer (CT), arises when an electron releasing substituent is suitably attached to an aromatic ring of a ketone. The charge may eventually migrate to the carbonyl oxygen producing a charge transfer state. Donor groups may typically be $-NH_2$, $-OH$ or = ;[30].

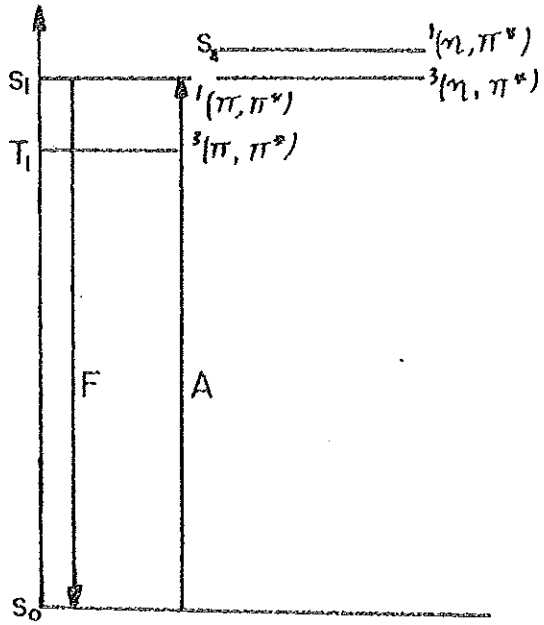
Assignment of the type of transition can be made by means of solvent effects[31,32]. If there is a blue shift in going towards more polar solvent, the transition is likely to be $n\rightarrow\pi^*$ If there is a smaller red shift, the transition



Type I



Type II



Type III

Fig. 2 Energy level diagram for transition in ketones

is likely to be n→π*. The shift of the n→π* transition occurs because the excited state is less strongely solvated than the ground state. The localized non-bonding electron of the ground state becomes delocalized on excitation over the less electronegative atoms around which the excited orbital extends. This is accomplished by a reduction in the

dipole moment of the carbonyl group and a consequent lowering of the interaction energy with the solvent. Further tests for identification of transitions which have an n- orbital may be summarized as:

1. The absence of a similar band in hydrocarbon analogues.
2. Disappearance of the band in strongly acid media where a proton combines with the lone pair of electrons
3. The presence of low intensity transitions relative to a typical transition.

2. Photoreaction of Ketones

All of the three types of excited states ($n \rightarrow \pi^*$), ($\pi \rightarrow \pi^*$) and (CT) have different electron distributions, hence exhibit differences in their photochemical reactivity.

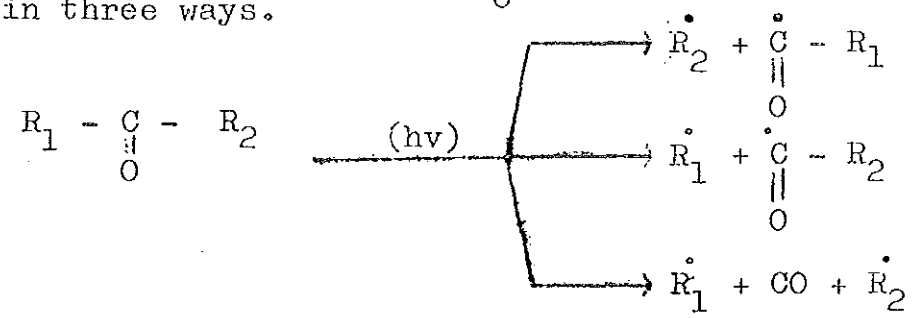
Intermolecular Photoreactions of Ketones

The three types of intermolecular reactions given by carbonyl compounds are decomposition, reduction and rearrangement.

a) Decomposition reactions

Carbonyl compounds undergo three types of photochemical decomposition reactions.

Norrish Type 1: Typical of ketones with no α-hydrogen. A carbonyl compound $R_1 - \underset{\underset{O}{\|}}{C} - R_2$ cleaves into free radicals in three ways.

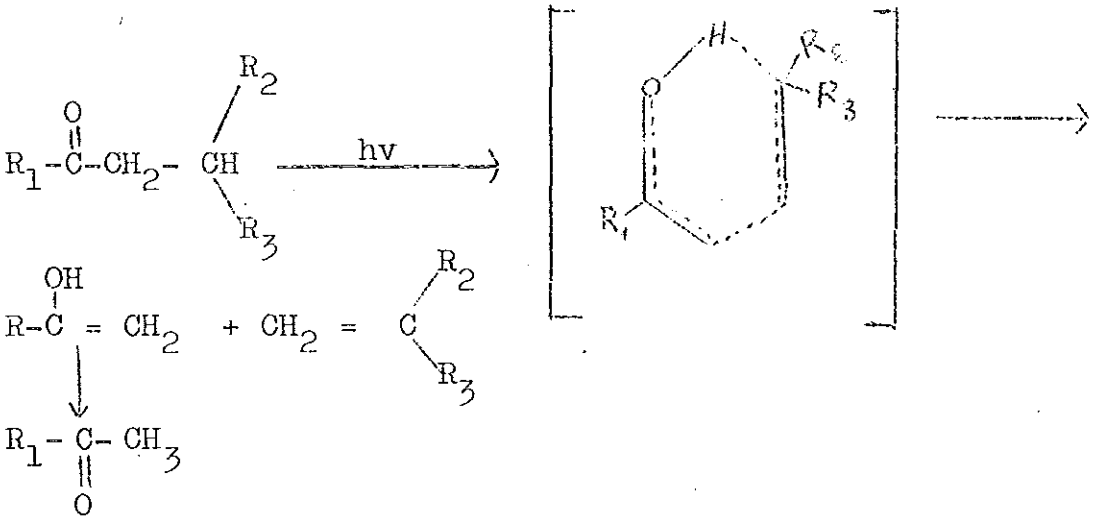


If R_1 and R_2 are different, one of the two proceses will be favoured over the other, the favoured process will involve the rupture of the weaker bond and formation of more stable radicals.

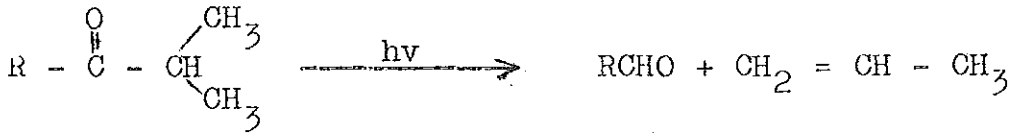
The free radical decomposition taking place in solvents is often prevented by the recombination of

radicals thus formed due to the cage effect of Solvent[35]. In the vapour phase the decomposition reactions become conspicous and the free radicals formed undergo secondary reactions.

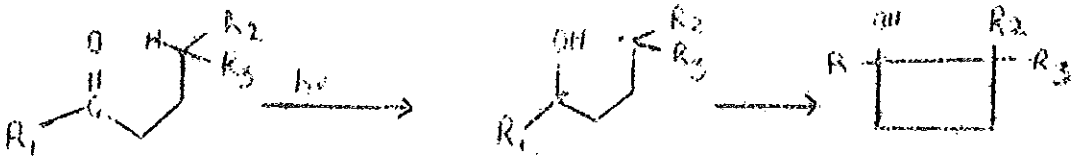
Norrish Type II:- This reaction type involves the decomposition of aliphatic aldehydes and ketone with γ-hydrogen in the alkyl chain. The mechanism of this reaction involves the cleavage of the γ-hydrogen by the excited carbonyl[33].



Norrish type III:- This is a photocycloelimination reaction which also yields one carbonyl and an olefin molecule. The mechanism probably involves cleavage of β-hydrogen, and is not as well investigated as the mechanism of type II reaction[37].



b) Reduction reaction: - The intermolecular reduction of the carbonyl group proceeds by the abstraction of a hydrogen atom from a γ-carbon. Formally the intermediate would be the same as that of Norrish type II decomposition but instead of fragmentation to an olefin, the biradical recombines to give a cyclobutanol derivative (15).[47-49]



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c) Rearrangment

Intramolecular rearrangements without reduction of the carbonyl group include. cis-trans isomerization of unsaturated compounds, ring closure, ring opening and ring contraction[33].

Intermolecular Photoreaction of Ketones

Carbonyl compounds undergo two kinds of intermoleular reactions: Photoreduction by abstraction of a hydrogen atom from another molecule, and dimerization.

The photoreduction process is significant in the light of the results obtained in this project and is, therefore, discussed in considerable detail hereunder.

Intermolecular Photochemical Reductions

In presence of an active proton donor, an excited carbonyl compound may accept a proton. In general, it is the solvent which acts as a proton donor and intermolecular photochemical reductions are observed in liquid phase only. Among the solvents that may be employed as hydrogen donors, alcohols and alkylbenzenes such as tolueneand cumene figure prominently.[44,42]

Insight into the photochemical hydrogen abstraction reactions of an $(n \rightarrow \pi^*)$ excited carbonyl group (16) can be obtained by considering the hydrogen abstraction reactions of alkoxy radicals. The RO radical (17) which possesses half-filled P orbitals may be a suitable model to predict reactivity pattern for hydrogen abstraction reactions.

16 17

From kinetic data for abstraction of hydrogen atom by RO radicals, the four factors listed below are expected to influence the reaction rate constant (kr), the hydrogen abstraction step.[43,44] These are

$$\dot{R}O + HX \xrightarrow{Kr} R - OH + \dot{X}$$

hydrogen donor — reduction product — radical

1) The strength of the bond broken and bond formed
2) Polar or charge-transfer effects on the energy of transition state relative to the energy of the reactants
3) Steric effects on the approach of the reagent and substrate
4) Solvent effects on the reagent, substrate, and transition state.

The activation energies (Ea) for intermolecular hydrogen abstraction range from 3-7 kcal/mole when the formation of the primary radical pair is exothermic from the initial n, π^* state[45]. It is important that certain restrictions are imposed on reactivity (as measured by kr, or Ea) by energetics on reactions involving diradicals since the reverse recombination reaction generally requires little or no activation energy in the absence of major resonance or steric effects, and since Ea cannot be less than ΔH for an endothermic reaction, it may be concluded that only exothermic reactions are likely to have Ea values small enough to allow reactions to be competitive with the other available, rapid modes of deactivation of excited states[46]. The contribution of a new OH bond to the overall reaction enthalpy, ΔH, will be constant since for a given ketone the same ketyl radical is formed in all cases. In general, overall abstraction of a saturated alcohol - OH, a benzene - H,

or a saturated alkane CH will generally be endothermic, thereby automatically providing a contribution to Ea. On the other hand, abstraction of hydrogen from the carbon α to the alcohol from a phenol OH, or from a tin hydride generally exothermic if the excitation energy $E \leq 70$ kcal/mole[47].

Other types of photochemical reactions which belong to this class of reactions are, photochemical dimerizations of α, β -unsaturated carbonyl compounds, and photochemical additions to olefins.

3. Quenching of excited singlet and triplet states of ketones by molecular oxygen

The interaction of molecular oxygen with electronically excited molecules leads to a number of physical and chemical transformation[49]. Molecular oxygen reversibly quenches both the excited singlet and triplet states.

Historically a number of different mechanisms have been proposed to account for the ability of oxygen to quench excited triplet and singlet states.

Kautsky has claimed that physical quenching of electronically excited state molecules by oxygen is related to sensitized photochemical oxidation reaction. This is based on studies on the photo-oxidation of spatially isolated sensitizer and acceptor molecules where it was

found that at low optimum oxygen pressure it was possible to selectively excite a sensitizer and produce oxidation on a distant acceptor molecule. The long range transfer of energy was due to the diffusion of the excited oxygen molecules which have been produced by quenching the phosphorescence of the sensitizer. The Kautsky energy transfer mechanism can be formulated as follows.

$$^3D_2 + {}^3O_2 \longrightarrow {}^1D + {}^1O_2 \qquad ({}^1\Sigma_g^+ \text{ or } {}^1\Delta_g)$$

where ^3D and ^1D represent D an excited triplet and ground singlet donor molecules respectively.[48,49] Energy transfer to oxygen is unusual only in that oxygen is initially in a ground triplet state and is excited to a metastable singlet state. A very significant feature of this mechanism is that electronically excited oxygen molecules are produced by the quenching process.

Another suggestion is quenching by the enhancement of intersystem crossing. In a series of experiments, Evans[51] demonstrated that oxygen reversibly enhances singlet - triplet (S → T) transition in organic molecules.

Hoijtink examined the possibility that an exchange interaction between the organic molecule and oxygen could lead to an enahncement of S → T transition in the organic molecule.

In their effort to explain the enhancement of the singlet-triplet transition by oxygen, Tsubomura and Mulliken[52] and Munell[53] have examined a mechanism which involves a charge transfer (CT) state of the organic - O_2 complex. It is generally believed that many organic ions quench the fluorescence and phosphorescence of organic molecules in solution by an electron transfer mechanism. By extrapolation, Weiss[54] proposed that oxygen quenching of phosphorescence might also be due to an electron transfer of the type

$$D^* + O_2 \longrightarrow D + O_2^-$$

where D* is an excited donor molecule. This model has been questioned by Tsubomura and Mulliken[52] on the grounds that complete electron transfer is unlikely in non-polar solvents.

Evans[51] and others suggested that an inhomogenous magnetic field produced by the paramagnetic gound - state oxygen molecule could cause some mixing of the singlet and triplet states of organic molecule and lead to enhanced intersystem crossing. Tsubomura and Mulliken[52] have theoretically evaluated the magnitude of this effect and have shown it to be of negligible importance. Furthermore, Porter and Wright[55] in their studies of quenching of triplet state by paramagnetic ions found no correlation between the quenching efficiency and the magnetic moment of the paramagnetic ions.

IV. EXPERIMENTAL

1. Purification of Solvents

Reagent grade benzene, toluene and xylene were dried over calcium chloride, filtered and further purified by distillation. The distillate which collected within a range of $1^{o}C$ was taken. Further drying, when necessary was achieved by placing the solvents over sodium wire and subsequent distillation as above.

Absolute ethanol was distilled before use. Propane-2-ol was refluxed over solid tin (II) chloride for 30 minutes to get rid of peroxides and refluxed over CaO for 4 hrs. It was distilled and the first portion of the distillate was discarded. The distillate was stored over 5A molecular sieve followed by further distillation.

Chloroform was shaken five times with about half its volume of water, then dried over anhydrous $CaCl_2$ for 24 hours and distilled.

Purification of Isatin

General purpose isatin (Hopkin and William) was used after recrystallization from benzene.

Gases used: - Nitrogen and Oxygen of about 96% purity (from SEDE) were used without further purification.

Preparation of N-methyl isatin

A 500 ml three necked flask was equipped with a separatory

funnel, a sealed mechanical stirrer and a reflux condenser. 7.35g of isatin was placed in the flask to which 2.5g of NaOH in 100 ml of water was added. The mixture was stirred and co. led to 10°C by immersing the flask in an ice bath. 6.3g of dimethyl sulphate in the separatory funnel was added dropwise during 1 hour whilst shrring the mixture vigorously. To complete the methylation it was heated under reflux for two hours and was filtered after cooling. The N-methyl isatin was recrystallized from water.

Periodic acid test - for the compound RFA - 2

One drop of concentrated nitric acid was added to 2.0 ml of a 0.5 percent aqueous solution of paraperiodic acid contained in a small test tube and the mixture was shaken well. 20 mg of the compound RFA (2) were introduced into the test tube and mixture was shaken and gently heated. The R_f value of the component formed was compared with an authentic isatin sample.

Bayer Villiger Oxidation of Isatin

A mixture of 10 ml of trifluoroacetic acid, 3 ml 30% H_2O_2 and 15 ml of methylene chloride was added over 15 minutes period to a well stirred mixture of 10 g of disodium hydrogen phosphate and 50 mg of isatin in 20 ml of methylene chloride. After addition was complete the

the mixture was heated under reflux for one hour. The products were compared by thin layer chromatography with the compound RFB - 1.

2. Solvent Effects on the Photo-reduction of Isatin

Seven organic solvents, chloroform, toluene, cumene, xylene, benzene, propanol, and ethanol were chosen for this study. .20 mg of isatin were dissolved in each of the solvents in 250 ml erlenmeyer flask. They were adjusted to approximately equal absorbance so that direct comparison could be made. Each of the isatin solution was purged and heremetically sealed under nitrogen atmosphere. The samples were exposed to unfiltered sunlight under identical geometrical conditions.

Samples were withdrawn from each solvent at intervals shown on the table below:

Sample No.	1	2	3	4	5	6
Time(minutes)	5	25	40	60	85	120

After withdrawing six samples the remaining solution of isatin was left until it completely faded and therefore formation of photoproducts was complete. The solvents were removed under reduced pressure until about 5 ml. were left.

The photoproducts were studied by thin layer chromatography using benzene 26, chloroform 66, n-hexane diethyl ether (80:20) 63 and acetone 5(A) as a developing solvent. The spots were visualized at 245 nm and also in iodine vapour.

3. The Effect of Various Atmospheres on the Fading Rate of Isatin ih Xylene

Isatin (50 mg) was dissolved in minimum anount of redistilled xylene. This was divided into 15 test tubes. Nitrogen gas was bubbled into each of the five test tubes at a pressure 516/in^2 for 10 minutes and the test tubes were immediately tightly closed.

For comparison under oxygen atmosphere, purified oxygen gas was bubbled into the solutions at a pressure of 516/in^2 for 10 minutes and the test tubes were immediately tightly dosed. The last five test tubes were sealed under normal atmosphere.

In every case during the exposure to unfiltered sunlight sufficient space was left in the test tube to insure as much contact as possible with the atmosphere above the solution in the test tubes. All the test tubes were exposed to sunlight in identical conditions.

One test tube from each atmosphere was withdrawn at intervals shown on the table below:-

Sample No.	1	2	3	4	5	6
Time(minutes)	15	25	40	60	85	100

After decomposition was complete the solvent was removed under reduced pressure until about 15 ml of each solution remained. Products were observed using thin layer chromatography. The solvent system (A) was used for developing. The spots were visualized at 245 nm, 325 nm and also in iodine vapour.

4. Isolation and Identification of the Photo-product

Isolation:-

Several erlynmeyer flasks of 5l capacity were used to dissolve the isatin in redistilled xylene in each flask. Each flask was bubbled with nitrogen for about 30 minutes before exposure to unfiltered sunlight. All the flasks were properly sealed. The exposure of the isatin solutions was done on a continuous basis to collect as much photoproduct as possible. Each flask was exposed for a period of one week. Large scale production requires the exposure as many as possible flasks to sunlight. From 500 mg of isatin 210 mg of photoproduct was collected (chemical yield 49%). The solution was filtered and a yellow

solid substance was obtained which was washed by ether and dried in an oven at 50°C. Two products were isolated by thick layer chromatography using the solvent system(A). The first component RFB-2 was recrystallized from benzene and the second component RFA-1 was recrystallized from acetone. The compound RFA-1 makes 95% of the total photoproduct collected.

Identification

In characterization of the photo-products of isatin classical and instrumental techniques were used according established procedures. Melting points were determined on a Unimelt apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 727E instrument, using KBr pellet. ^{1}H-NMR spectra were recorded on a Varian T-60A NMR spectrometer at 60MHz, using deuterated acetone, trifluoroacetic acid and dimethyl sulfoxide as solvents. Tetramethyl silane was used as a reference compound. UV-Vis spectra were recorded on a Sp 8 - 100 pye Unicam and Perkin-Elmer model 727E double beam spectro-photometer.

5. Determination of Reaction Quantum Yield

In order to have some idea about the efficiency of the photoreaction it was necessary to determine the reaction quantum yield. 0.20 mg. of isatin was dissolved

in cumene and its absorbance was adjusted to be equal to that of the actinometer in cumene. Both were purged with nitrogen for 10 minutes and were carefully sealed. The actinometer and the sample. were irradiated using a monochormater with a mercury lamp at 436 nm and the reaction was followed by measuring the absorbance with a uv-visible spectrophotometer.

V. RESULTS AND DISCUSSION

1. Solvent Effects on Photoreaction of Isatin

Since it was observed that the solvent plays an active role on the photoreaction a detailed study was undertaken. Two sets of solvents were selected for this study. In the first set were benzene, toluene and xylene - in which the ease of abstraction of hydrogen gradually increases. The second set consisted of cumene and isopropyl alcohol, having comparable ease of hydrogen abstraction but a wide difference in polarity. Toluene was added to this group to make comparison with the first group possible.

Isatin was dissolved in each of these solvents and each set was adjusted to approximately equal absorbance to make direct comparison possible. To eliminate the already known effect of oxygen, inert nitrogen atmosphere was used (vide infra). The photoreaction in each solvent was followed by measuring the absorbance. From a plot of absorbance vs time Fig. (3) and Fig.(4) $E_{1/2}$ (the time necessary for the absorbance to decrease by half) was found to be as follows:-

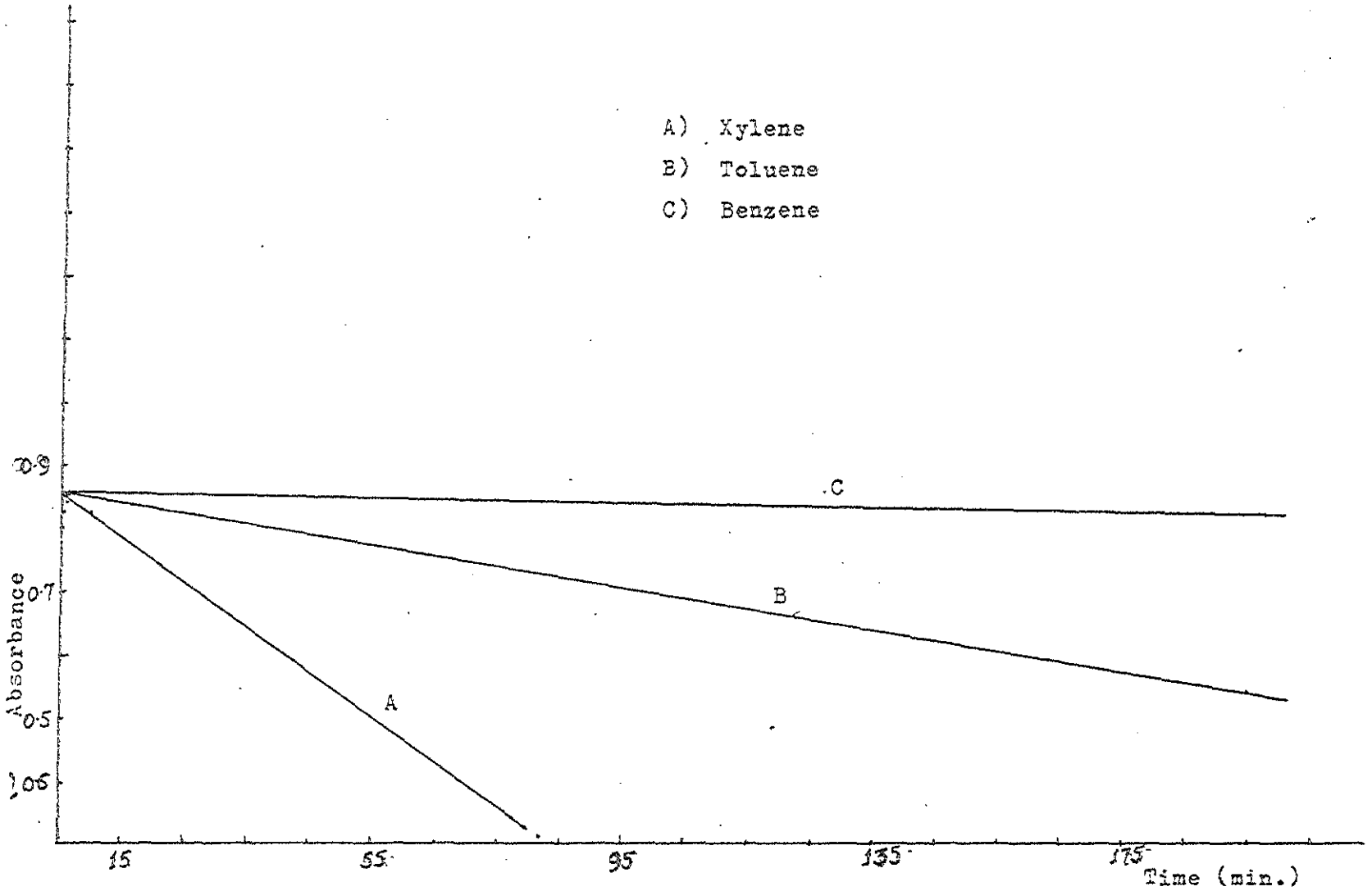


Fig. (3) The fading rate of isatin in benzene toluene and xylene.

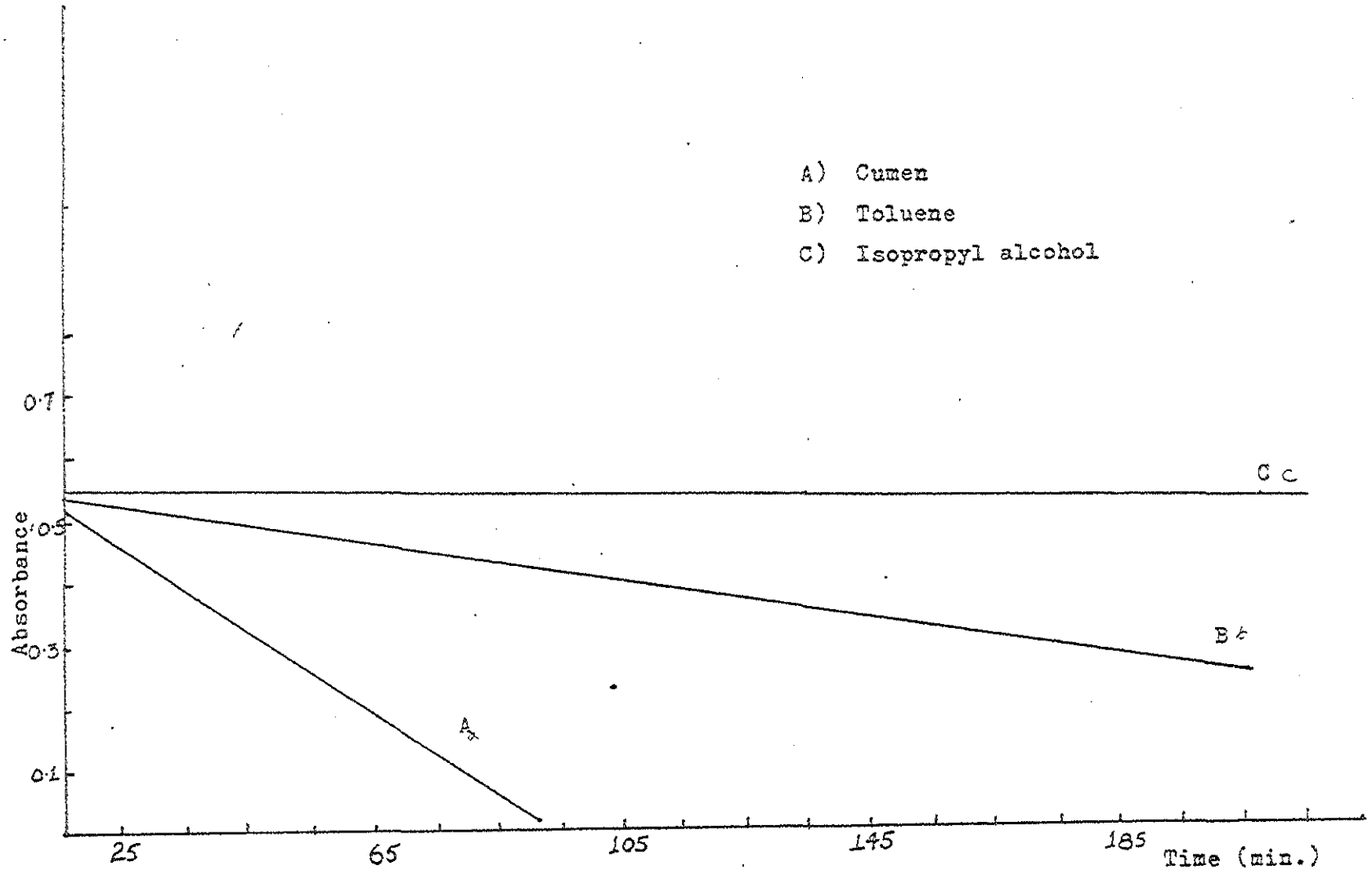


Fig. (4) The fading rate of Isatin in cumen, isopropyl and toluene

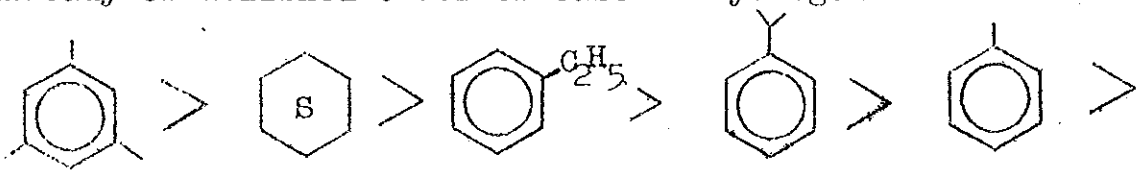
Set 1		Set 2	
Solvent	$E_{1/2}$	Solvent	$E_{1/2}$
Benzene	126 min	Isopropyl alcohol	very long
Toluene	102 min	Toluene	175 min
Xylene	68 min	Cumene	44 min

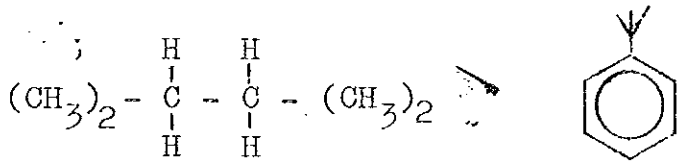
From these results it can be seen that the rate of photoreaction decreases with increase in polarity of the solvent and decrease in ease of hydrogen abstraction.

At least two possible explanations can be speculated. i) The equilibrium constant for such a reaction is small and therefore the reaction will stop after a very short time unless there is a means of taking the photoproducts from the solution. In the nonpolar solvents since the solubility of the photoproducts is very low the phoroporoducts precipitate out of the solution and the reaction can proceed to a relatively larger extent before coming to equilibrium. In the polar solvents, however, the phtoproducts are soluble to a larger extent and therefore equilibrium is reached at a very early stage of the reaction such that the reaction proceeds to a very negligible amount in ethanol and isopropyl alcohol.

ii) The above speculation does not explain why for example the rate of the reaction is faster in chloroform than in ethanol where there was no formation of precipitate in either solvent.

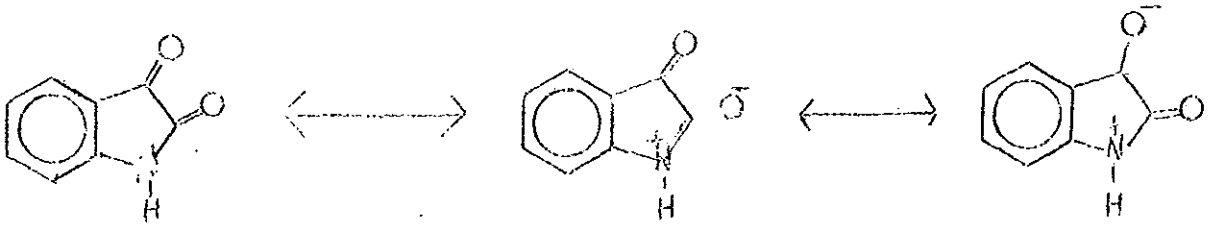
From the $F_{1/2}$ values it can be seen that the rate of fading in the hydrocarbon solvents follows the ease of hydrogen abstraction as can be seen by comparison with the already established order of ease of hydrogen abstraction.[58,59]





The fact that the reaction proceeds to a very negligivle extent in isopropyl alcohol, which is a good donor of hydrogen atom, suggests that as the polarity of the solvent is increased the charge transfer character of the $n \rightarrow \pi^*$ transition becomes dominant. This formation of the excited state with separation of charge should be in accord with simple electostatic theory leading to stabilization of those states by polar solvents. In these polar solvents, therefore, intramolecular charge

transfer from the electron donating nitrogen to the acceptor carbonyl group will be enhanced.



This electron shift has an effect of reducing the electrophilicity of the carbonyl oxygen in the excited state and makes it more nucleophilic. Thus the reactivity of the excited states toward hydrogen abstraction is greater in the $n \rightarrow \pi^*$ than in the charge transfer transition. This explains why the rate was much slower in isopropyl alcohol which is a good donor of hydrogen atom.

Additional support for this explanation comes from the following experimental findings.

1. The maximum wavelength of absorption in isatin has been shown to be $n \rightarrow \pi^*$ transition. This is supported by the following observations:

   a) Addition of an acid gradually decreases the band of the wavelength of maximum absorption because the nonbonding electrons are tied up with the added hydrogen ions and are not available for excitation hence disappearance of this band.

b) The absence of a similar band (at about 400 nm) in indole (the hydrocarbon analogue of isatin) indicates that this band must be due to the carbonyl group.

A blue shift in going to more polar solvents would have been expected for a $n \rightarrow \pi^*$ transition because the unshared electrons of the n orbital can be solvated by a polar solvent: the ground state is thus stabilized and the transition energy increases. Accordingly, the absorption wavelength in a polar solvent will be shorter than in a non-polar solvent. The fact that red shift is observed in going to more polar solvent supports the conclusion that a change in transition from $n \rightarrow \pi^*$ to charge transfer occurs.

2. An attempt was also made to make the lone pairs of the nitrogen more and less available for charge transfer than in isatin by studying the fading rate of N-methyl and N-acetyl derivatives of isatin respectively. Solutions, of isatin, N-acetyl isatin and N-methyl isatin in xylene were prepared and the concentrations adjusted to the same absorbance and purged with nitrogen. The photoreaction was followed by measuring the absorbance at different times. From a plot of absorbance Vs time the following values were evaluated:

A) N - acetyl isatin

B) Isatin

C) N - methyl isatin

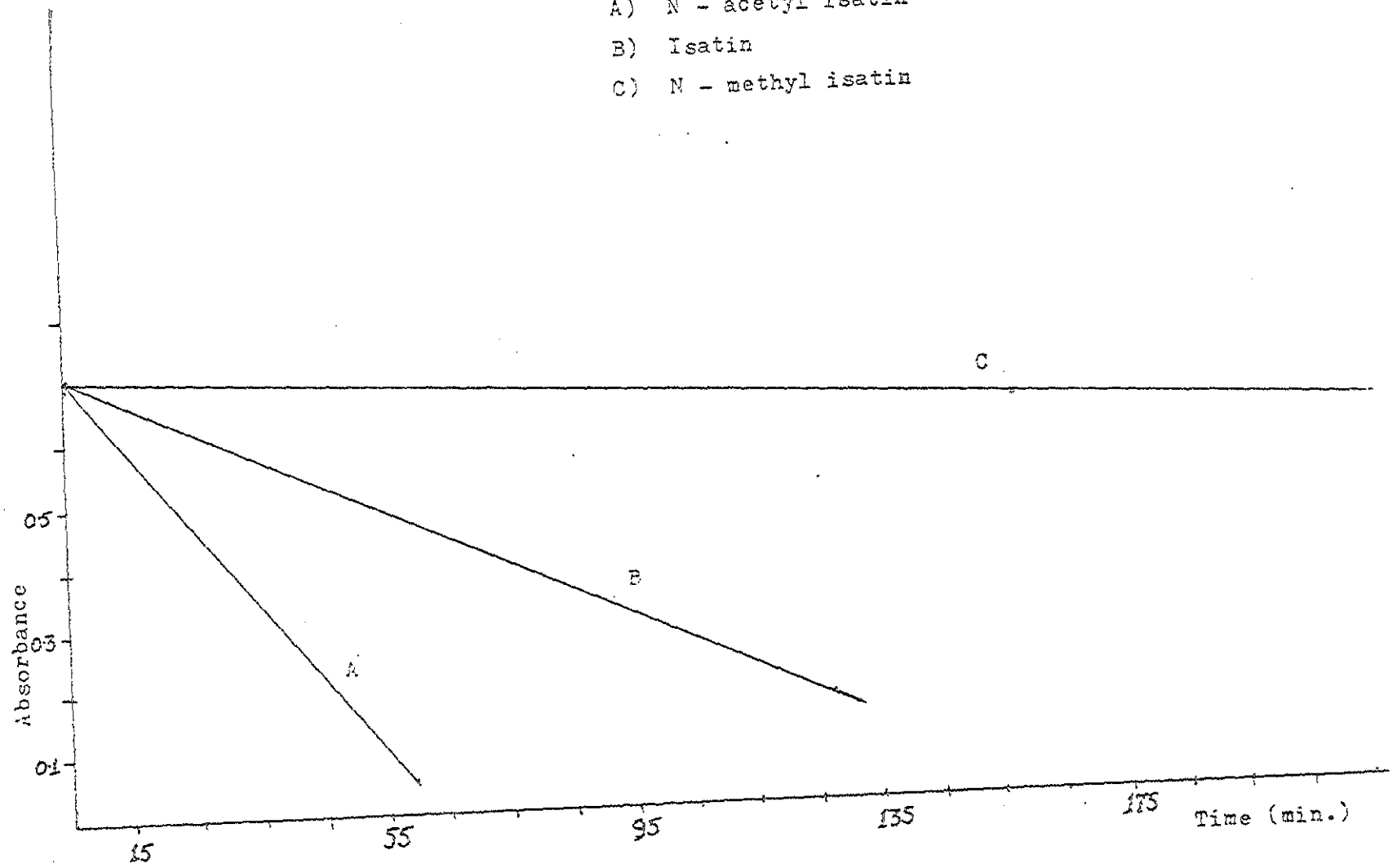


Fig. (5) Comparative fading rates of Isatin, N - acetyl Isatin and N - methyl Isatin

Substance	$E_{1/2}$ (minutes)
N-methyl isatin	Very long
Isatin	85 minutes
N-acetyl isatin	35 minutes

As expected the rate of fading was fastest for N-acetyl isatin where CT is less probable and slowest in N-methyl isatin where CT transition is expected to predominate. As expected isatin has an intermediate rate.

The probable conclusion that "state switching", i.e the reversal of an initial energy disposition, was achieved by variation in ketone structure and solvent polarity.

2. Effects of Different Atmospheres on the Photoreaction of Isatin

Molecular oxygen is known to quench both the excited singlet and triplet states of organic molecules[60,61]. To see the effect of molecular oxygen in the photoreaction of isatin a solution of isatin in xylene was exposed to unfiltered sunlight under three different atmospheres, oxygen, nitrogen and air. The reaction was followed by measuring the absorbance at different times.

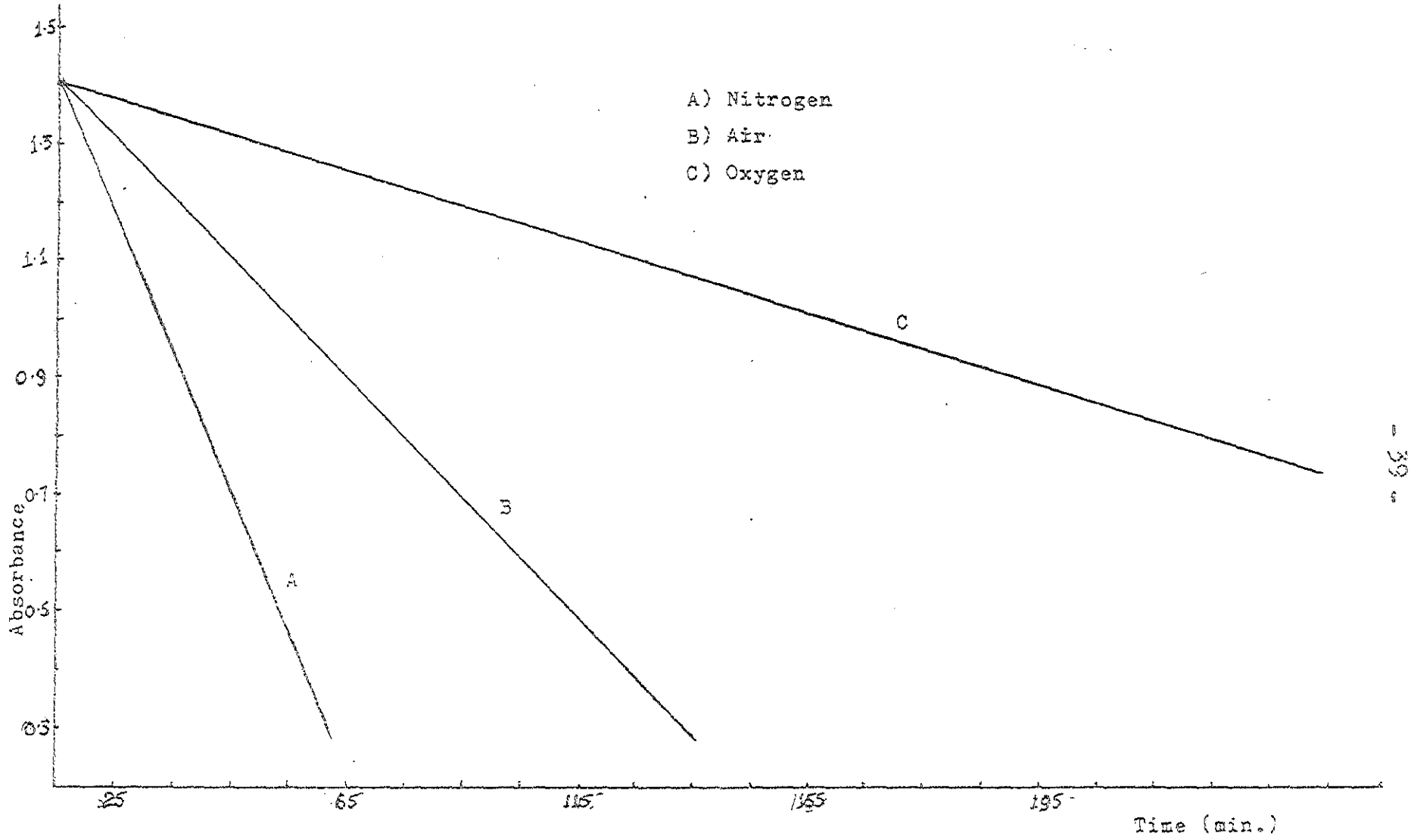


Fig. (6) Comparative fading rates of Isatin under different atmospheres.

From a plot of absorbance Vs time (Fig. 6) the following $E_{1/2}$ values were obtained.

Atmosphere	$E_{1/2}$
Oxygen	245 minutes
Normal air	111 minutes
Nitrogen	45 minutes

From these results it is clear that the fading rate is fastest in nitrogen atmosphere (i.e. at very low oxygen concentrations) and slowest in oxygen atmosphere. A possible conclusion is that molecular oxygen acts as a quencher in this photochemical reaction. It is important to note that this quenching could be observed not only in xylene as a solvent but in any organic solvent where photoreaction is possible.

Comparison of the products formed under the different atmospheres using thin layer chromatography indicates the formation of the same set of products. Two products were found in all cases. The only difference observed was the relative amounts of the products i.e. as the amount of oxygen was increased the amount of major product decreased while the minor product increased.

3. Fluorescence of Isatin

Both the excited singlet and triplet states possess a great deal of excess energy (between 40 to 200 kcal/mole). Their energy is often enough to overcome activation barriers so that chemical processes can take place. When reactions do not occur the excess energy is lost through a variety of ways. The several modes of deactivation open to the excited states may be divided in radiative and non-radiative processes. Two types of emissions from radiative deactivation are recognized. The type associated with the excited states may be divided in radiative and non-radiative processes. Two types of emissions from radiative deactivation are recognized. The type associated with the excited singlet to ground state singlet emission is fluorescence while that associated with triplet to gound state singlet deactivation is phosphorescence[62,63].

A dilute solution of isatin in benzene was prepared in order to take the fluorescence spectrum of isatin. The λmax for absorption of isatin in benzene solution occurs at 401nm while the λ max of fluorscence emission for isatin in benzene is 454 nm. A possible explanation for such a shift is that when the molecule changes to the excited state by the absorption of energy the relationship between the solvent and solute is upset. An excited solute molecule in this

situation is in the Franck - Condon state. This state prevails for very brief period of time, and the solvent molecules cannot reorient themselves during the transition from the ground and excited states and thus will be reflected in changes in absorption and emission spectra.

A contribution to such a shift might come also from differences in the geometry of the ground and excited states.

Since the reaction quantum yield decreases with increase in concentration of oxygen (i.e oxygen quenches the reaction) it was hypothesised that if fluorescence decreases with increase in oxygen concentration then the reaction could be starting from either the excited singlet state or excited triplet state or even both states. If however, fluorescence does not decrease with increase in concentration of oxygen then the reaction must be starting from the triplet state.

From the series of experiments done on fluorescence at different concentrations of oxygen it was not possible to trace unambigously the spin state from which the reaction starts.

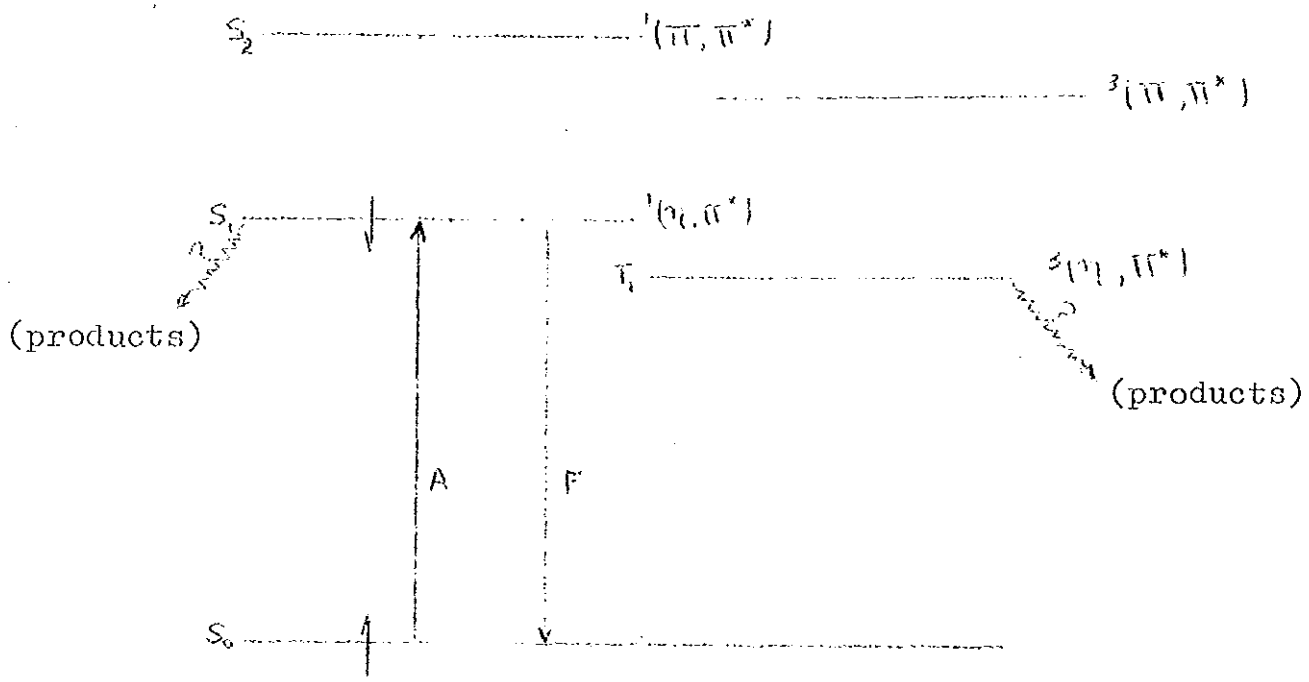


Fig.(7) Energy level diagram for isatin

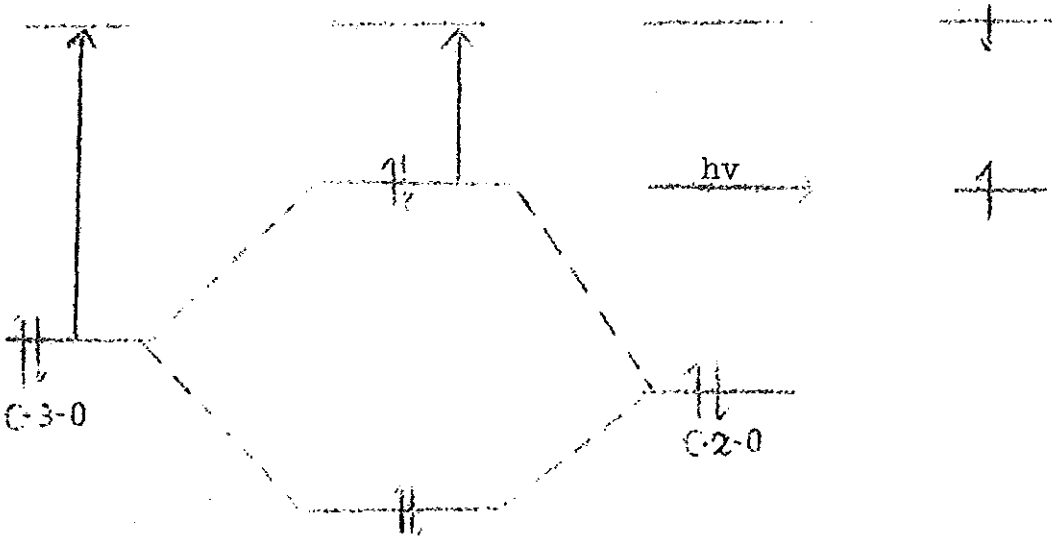
4. Isolation and Identification of the Photoproducts

a) The possible Photoproducts of Isatin

Before making any theoretical predication on the different possible photoreactions isatin can undergo it is essential to construct its energy level diagram.

Isatin is an α-dicarbonyl compound, the energy of these two carbonyl groups is different due to differences in their environment. The C-2 carbonyl group is attached to a nitrogen atom which has an effect of weakening the π -bond while strengthening the σ -bond of this carbonyl group.

The two carbonyl groups interact both through the bonds and space. This interaction of the atomic orbitals gives rise to orbitals of higher and lower energy. Though the overall energy does not change, as can be seen from the energy level diagram, this has a dramatic effect on the wavelength of maximum absorption.



Energy level diagram for isatin showing the effect of interaction of the adjacent carbonyl groups.

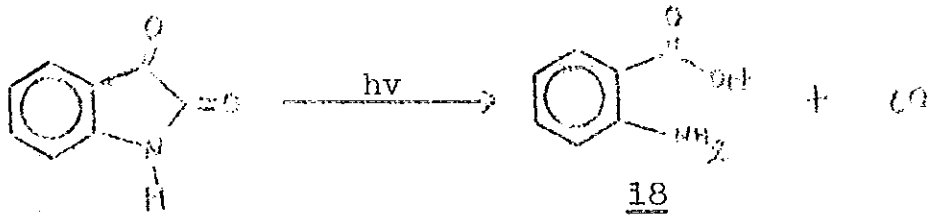
It can be seen that wavelength of maximum absorptions has been greatly increased compared to the case of a single carbonyl group.

Although it would not be possible to predict the exact nature of the photoproducts of isatin in any given solvent, it would be reasonable to enumerate the set

of possibilities by comparisons with α-dicarbonyl compounds.

1. The primary process in the photolysis of many α-dicarbonyl systems is the scission of the low energy CO - CO bond.[64-66] A typical example would be the photolysis of pyruvates in benzene resulting in the formation of acetaldehyde, CO, and carbonyl derivatives corresponding to the O-alkyl group.

Writing such a reaction for isatin gives the aminoacid 18.



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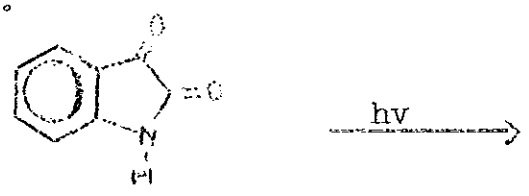
Indeed the lactone 19 is reported to yield the acid 20

19 20

2. α-cleavage followed by addition of water would give two different products (21 and 22) depending on the site of cleavage.



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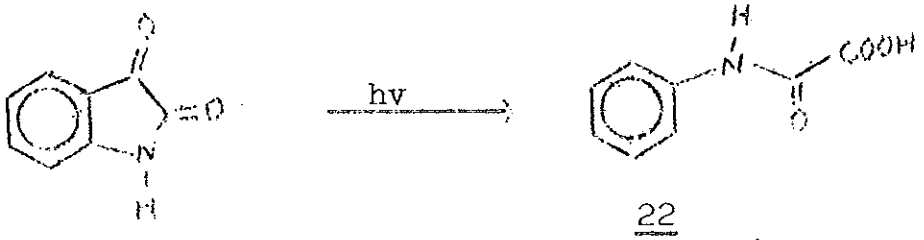

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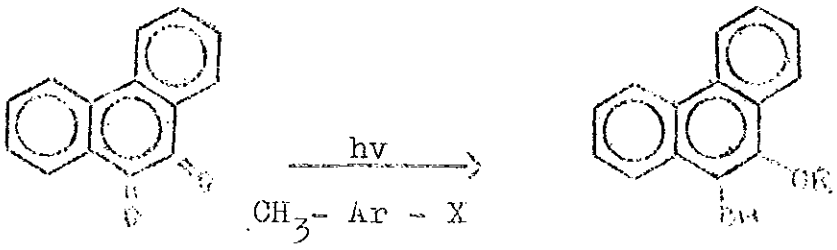
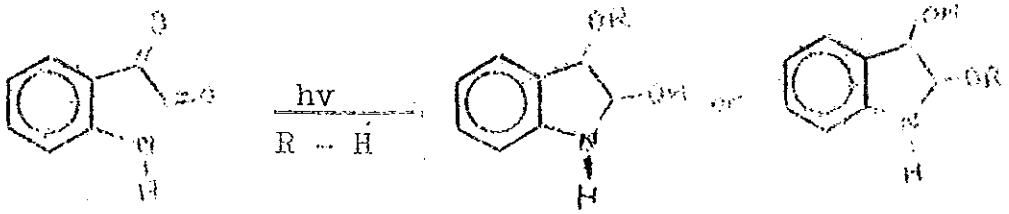
3. 1.2 addition:- Rubin[67] studied the 1.2 addition of substituted toluenes to 9,10 phenanthroquinone.

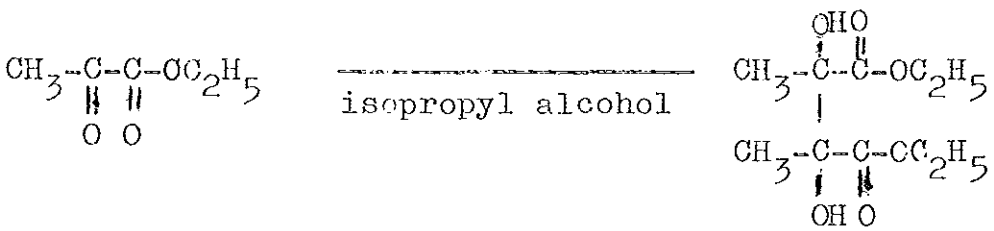


An analogous reaction for isatin would give (23) and/or (24)

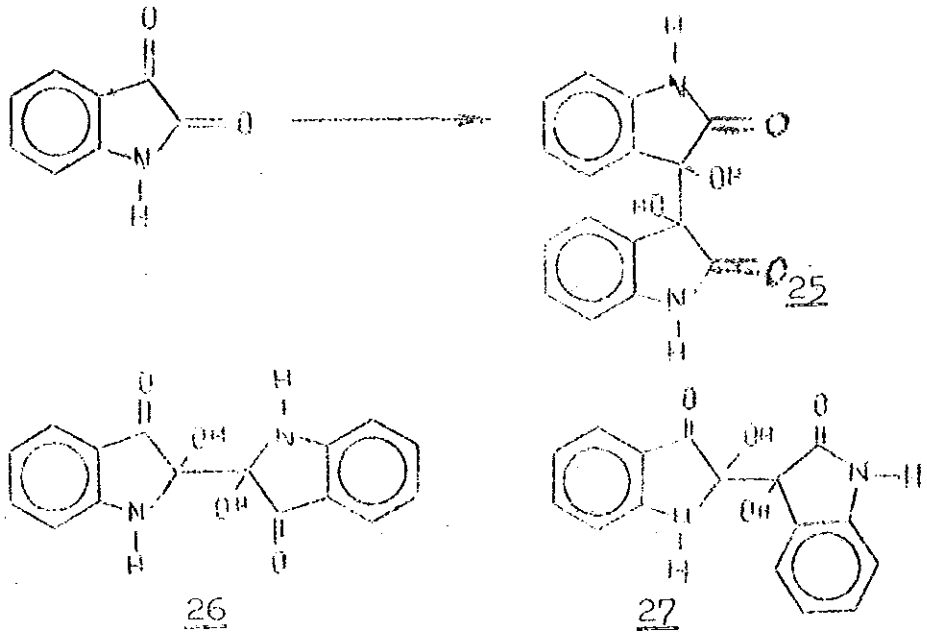


23 24

4. Photoreduction - the use of solvent that facilitates hydrogen abstraction such as isopropyl alcohol leads to the formation of pinacol[68].



In the case of isatin there are three possibilities



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An analogous reaction for isatin where only the keto group (C-3) undergoes photoreduction would give rise to the pinacol (25). However, if photoreduction of the other carbonyl (C-2) occurs as well, then one would expect (26) and the crossed product (27).

b) Spectroscopic Properties of Isatin

Since the proposed structures of the photoproducts incorporate, in part, the isatin moiety the IR, NMR and Mass spectra of isatin discussed below, were used in the interpretation of the spectra of the products.

1. ^{1}H-NMR - DMSO was used as a solvent. Only the aromatic protons are observed.

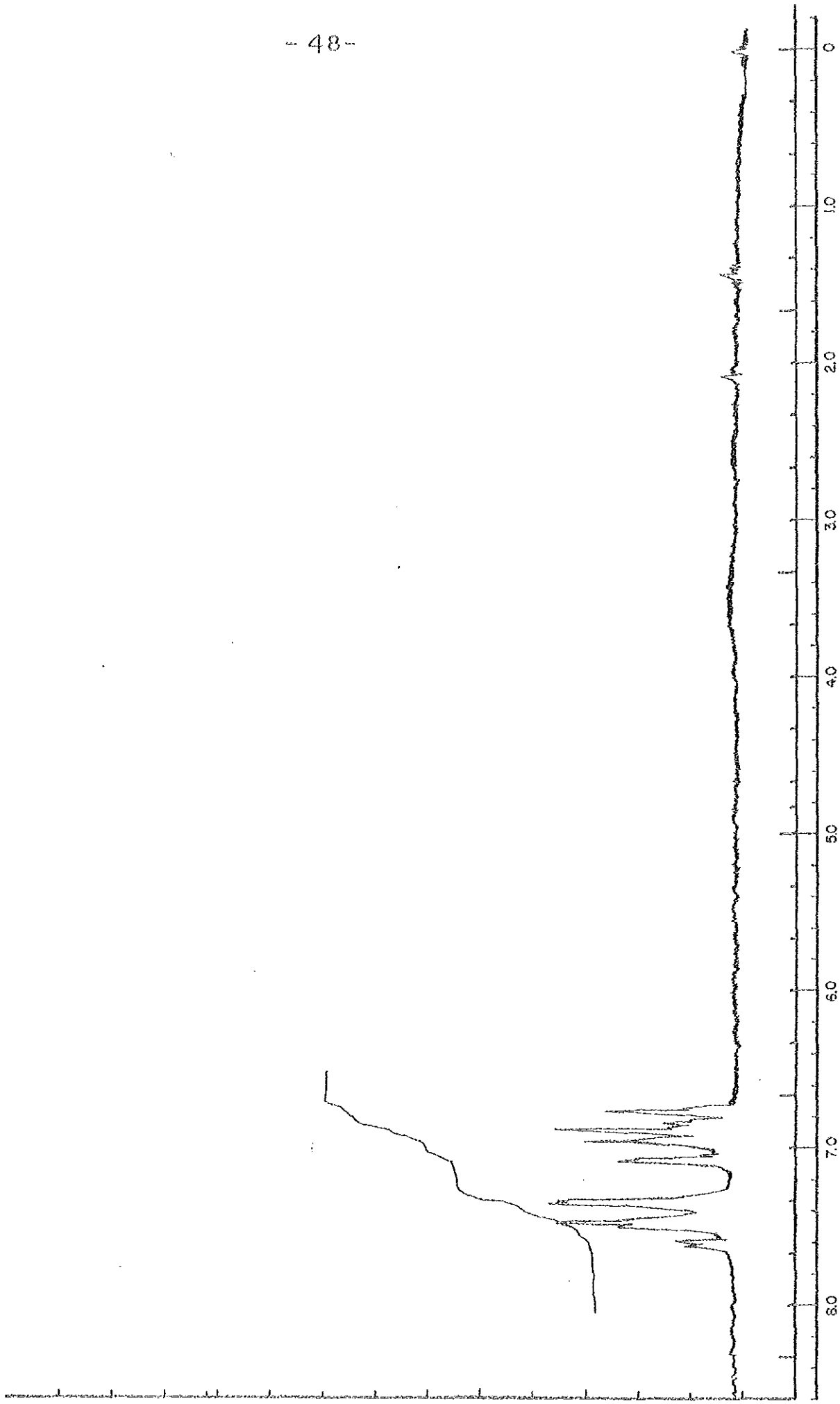


Fig. (8) NMR Spectra of Isatin

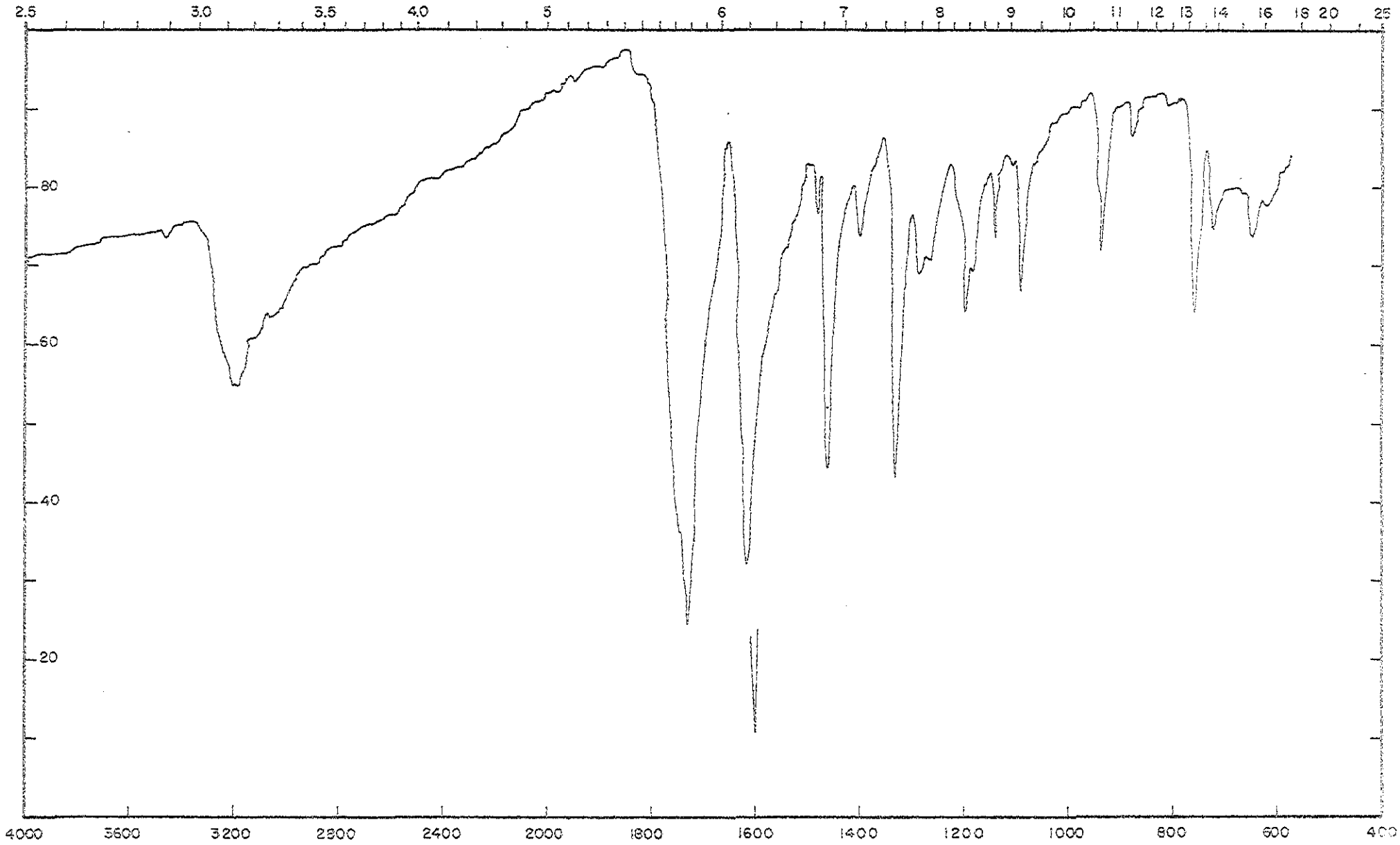
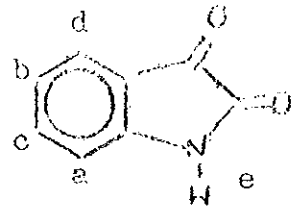


Fig. (9) IR Spectra of Isatin



Proton	Chemical shift
a	6.65 ppm
b	6.8 ppm
c	7.5 ppm
d	7.65 ppm
e	unobserved

2. IR

The absorption at 3200 cm^{-1} could be assigned to the N-H stretching with characteristic amide pattern. Absorption at 760 cm^{-1} is due to N-H wagging while the peak at 1460 cm^{-1} is the amide carbonyl group stretching frequency while the peak at 1620 cm^{-1} is due to the other carbonyl group both mechanically coupled to each other.

The sharp absorption at 1335 cm^{-1} is due to C-N stretching vibration.

The absorption at 650 cm^{-1} is characteristic of 1, 2 substituted benzene ring.

3. Mass - spectra

The molecular ion peak is the intense peak at (m/e = 147). Loss of a CO group gives rise to the peak at (m/e = 119) while loss of the two CO groups gives rise to the signal at (m/e = 91).

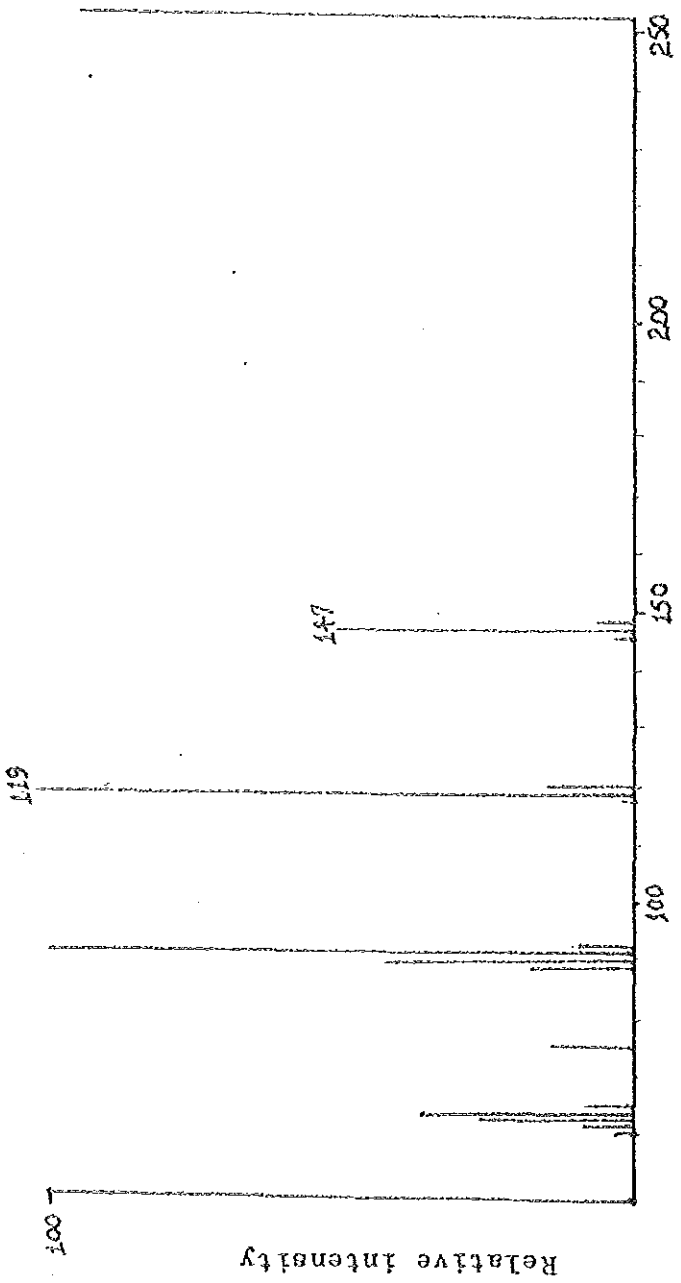
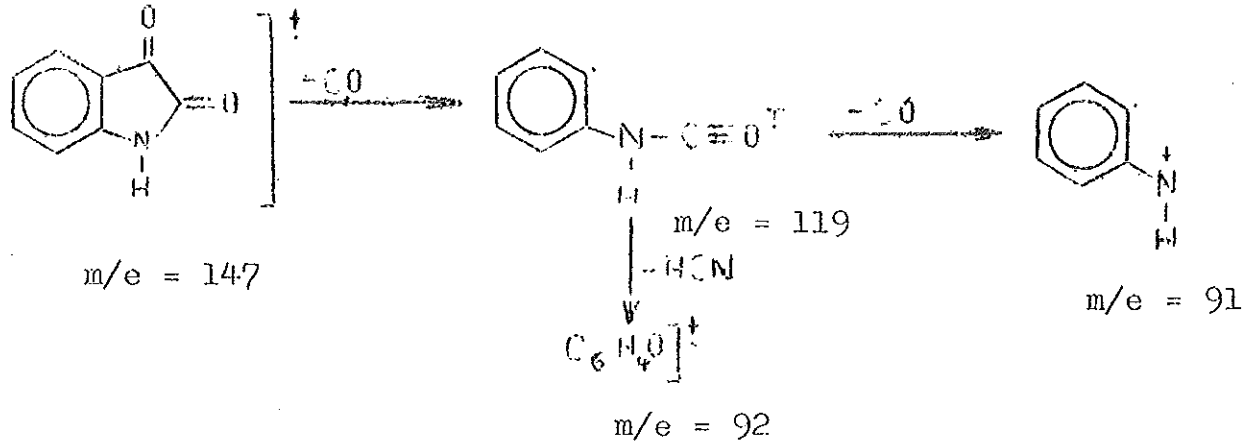


Fig. (C) Mass Spectra of Isatin

A loss of HCN from the fragment at (m/e = 119) gives rise to the fragment (m/e = 92).



c) Isolation and Identification of the Photoproducts

Isatin dissolved in xylene and under nitrogen atmosphere was exposed to unfiltered sunlight. A yellow solid substance was collected from which two solid components were isolated by preparative thin layer chromatography using solvent system (A) developing. The first compound (RFB - 1) was recrystallized from benzene and the other compound (RFA - 2) was recrystallized from acetone.

Identifications of these products was made mainly by spectroscopic means and a brief summary is presented.

Co pound - RFB (1)

This is a reddish brown compound recrystallized from benzene which has a melting point of 226 - 227°C. It is insoluble in non-polar solvents but moderately soluble in chloroform and soluble in acetone and ethanol. This

component can be approximated as 5% of the total product.

Identification

1. Elemental analysis gave

   Found %C = 58.94; H = 3.83; N = 8.50;

   Calculated % C = 58.90; H = 3.09; N = 8.59

The elemental analysis suggests the empirical formula $C_8H_5NO_3$. This was confirmed by accurate mass measurement from the high resolution mass spectra. (Found 163.0268, Calculated 163.029).

2. IR : Multiple absorbance between 3300-2900 cm^{-1} is due to an N-H stretching vibration characteristic of an amide group. For comparison the spectra of indigo Fig(17) and isoindigo Fig(16) are included. Such a characteristic pattern is observed only in isoindigo which has an amide group.

The intense double absorbances at 1765 cm^{-1} and 1728 cm^{-1} are assigned to carbonyl groups coupled to each other.An intense absorption at 750 cm^{-1} could be due to an out of plane wagging of N-H in accordance with the same phenomena being seen in lactam between 800 - 700 cm^{-1}. The sharp absorption at 680 cm^{-1} is assigned to the skeletal vibrations of benzene ring. The very weak absorption at 3010 cm^{-1} could be assigned to an aromatic C-H streching vibration frequence.

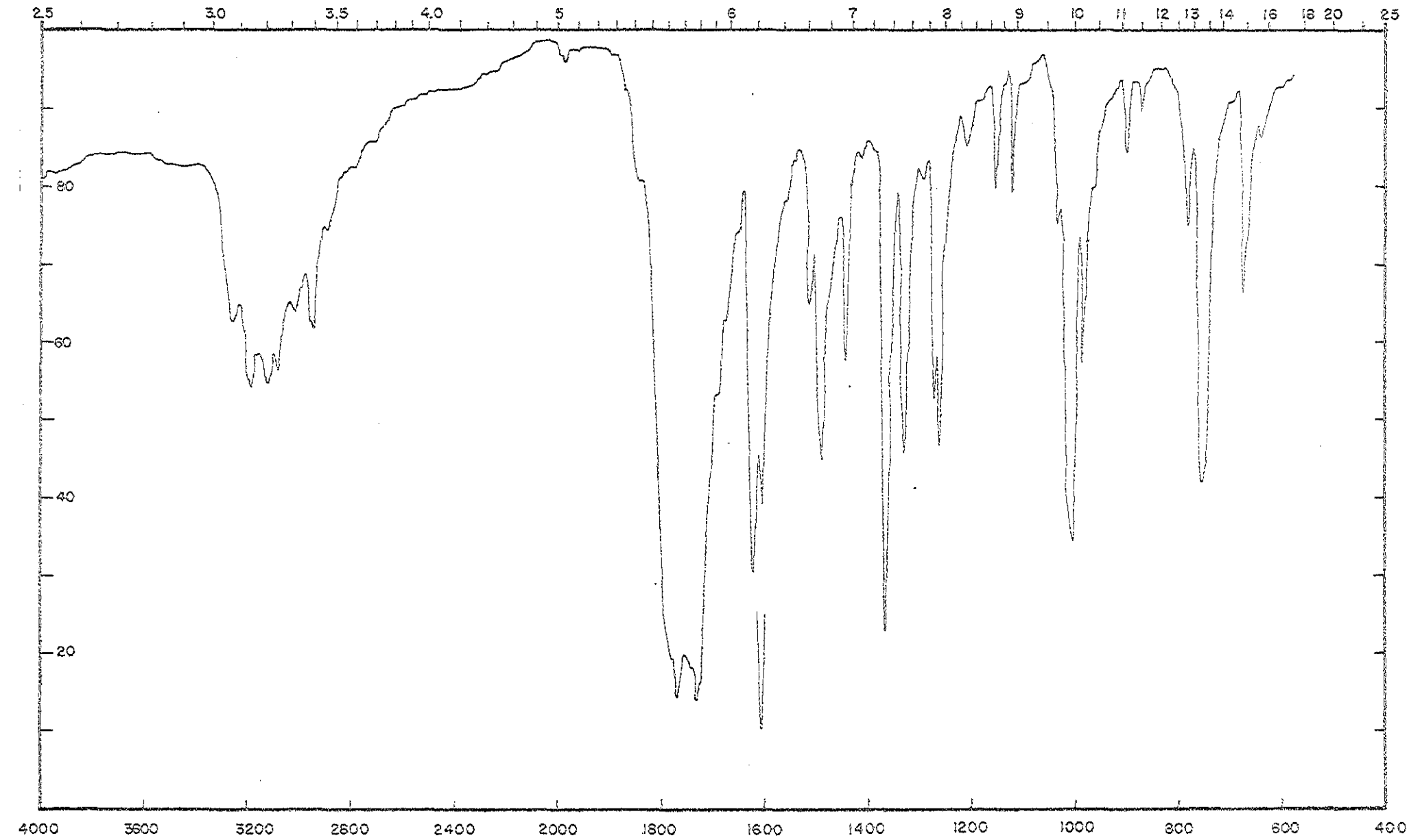
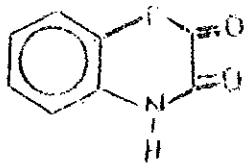


Fig. (II) IR - Spectra of compound RFB - 1

3. ^{1}H-NMR. The compound was dissolved in deuterated acetone.

The signals between δ = 7.0 ppm - 8.0 ppm are assigned to aromatic protons. From the pattern of the aromatic proton signals it can be seen that the benzene ring is a 1, 2 substituted which is in argeement with the IR spectral data. The signal at (δ = 3.0 ppm) is assigned to an N-H proton. The moderate broadness is characteristic of N-H which may undergo exchange. From the integration curve the ratio of the N-H proton to aromatic protons is 4:1. An additional nmr of the sample was also run in trifluoroacetic acid and as expected to N-H proton disappeared from the (δ =0 - 10 ppm) range. It was possible to confirm the signal at (δ =2.00 ppm) was a side band by varying the spinning rate and observing the change in the signal. The signal at (δ = 2.34 ppm) is due to contamination with acetone this can be confirmed by running the nmr with trace amounts of acetone.

The combined IR, NMR and mass spectra data suggests the following structure.



2,3 dioxo-1,4-benzoxazine

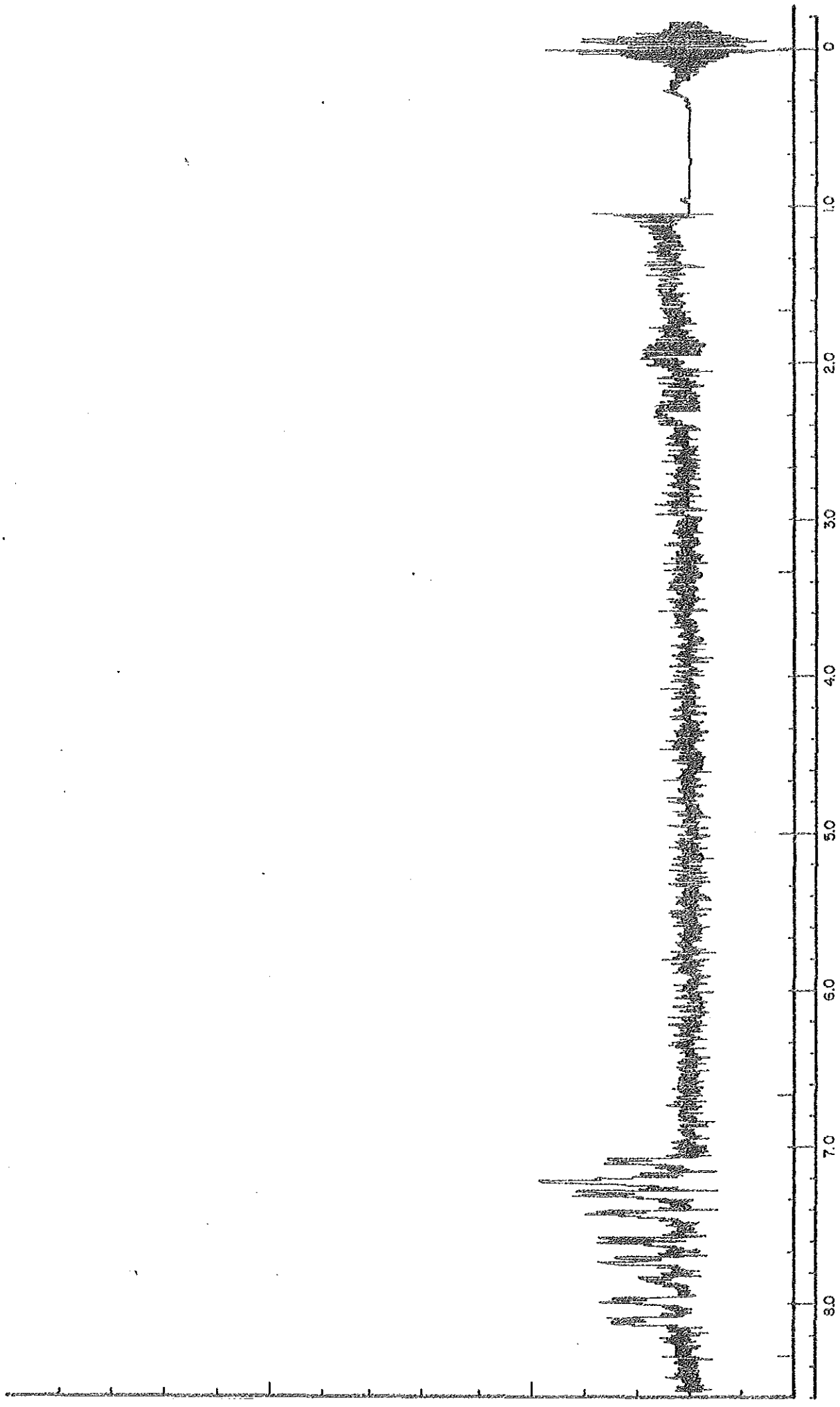


Fig.(12) NMR Spectra of RFB-1 in trifluoracetic acid.

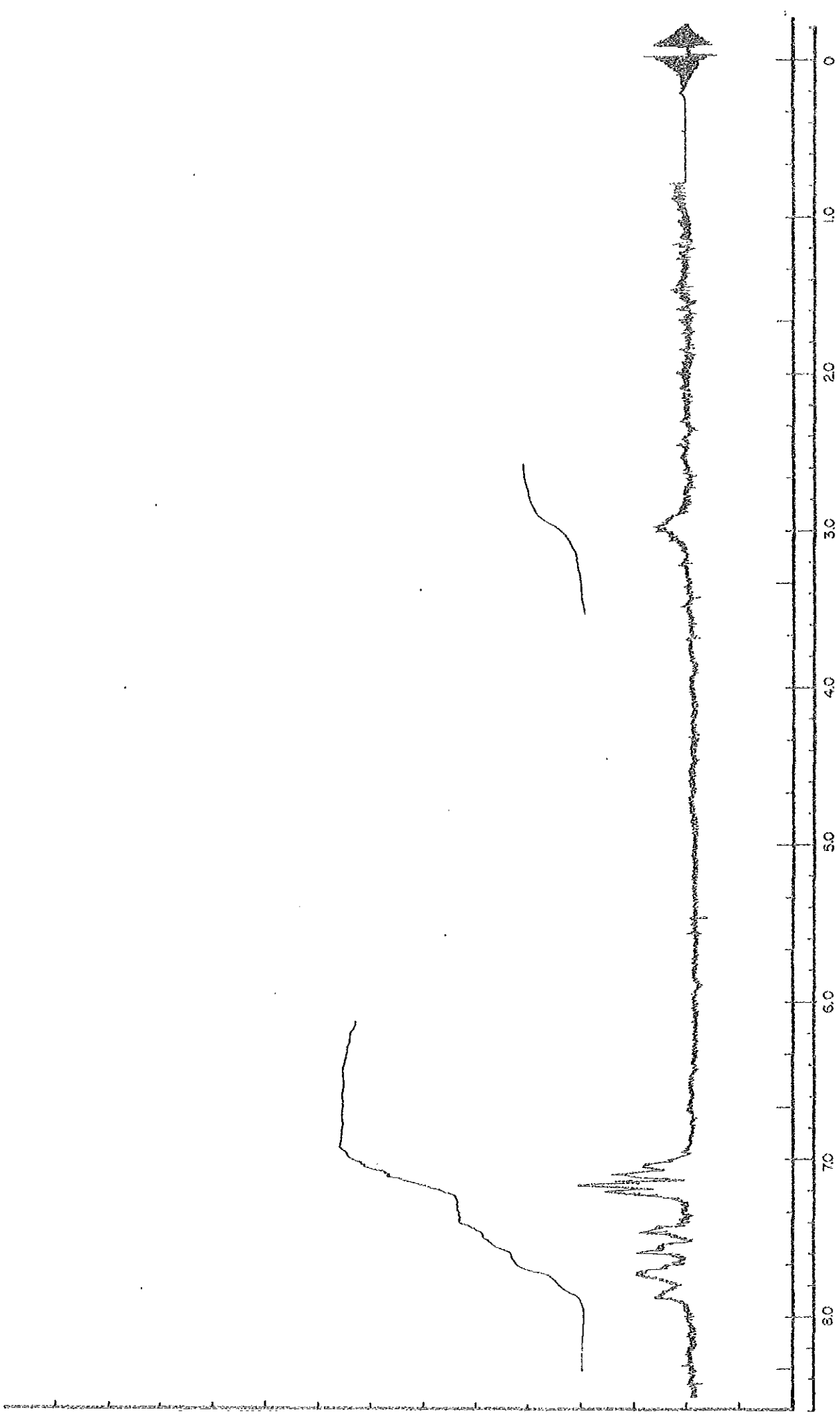


Fig. (13) NMR Spectra of RFB - I in deutrated acetone

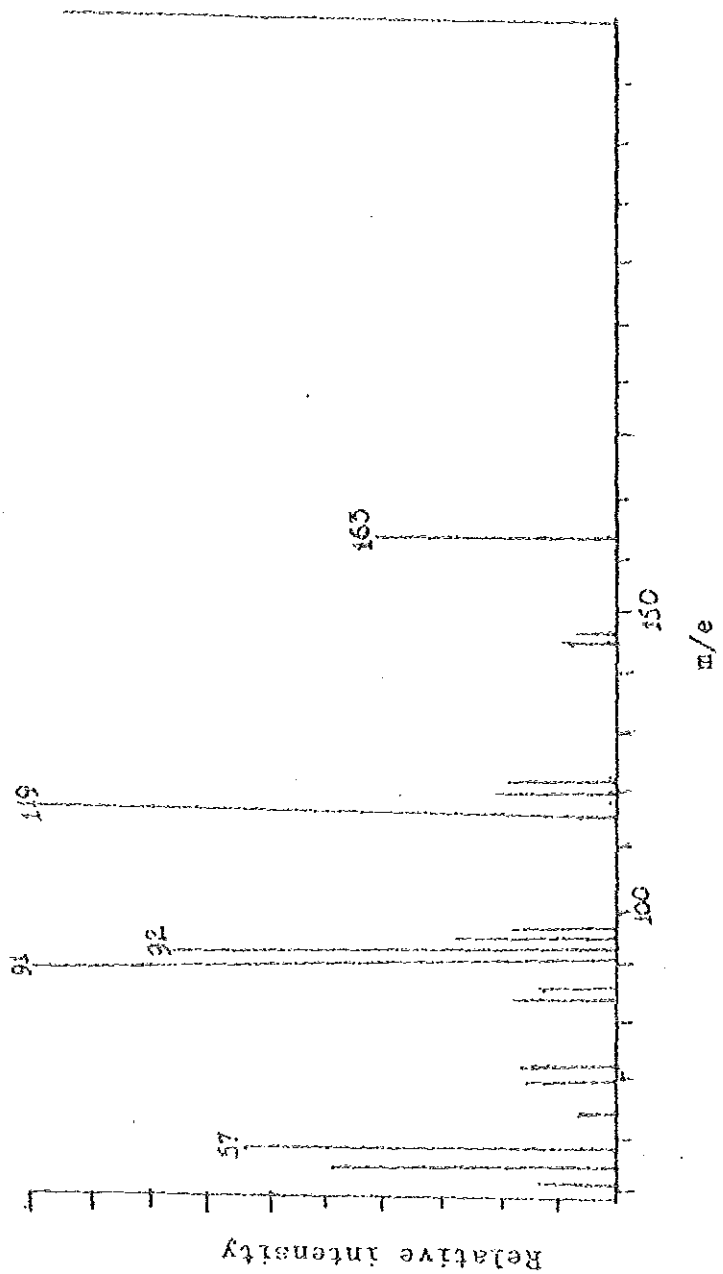
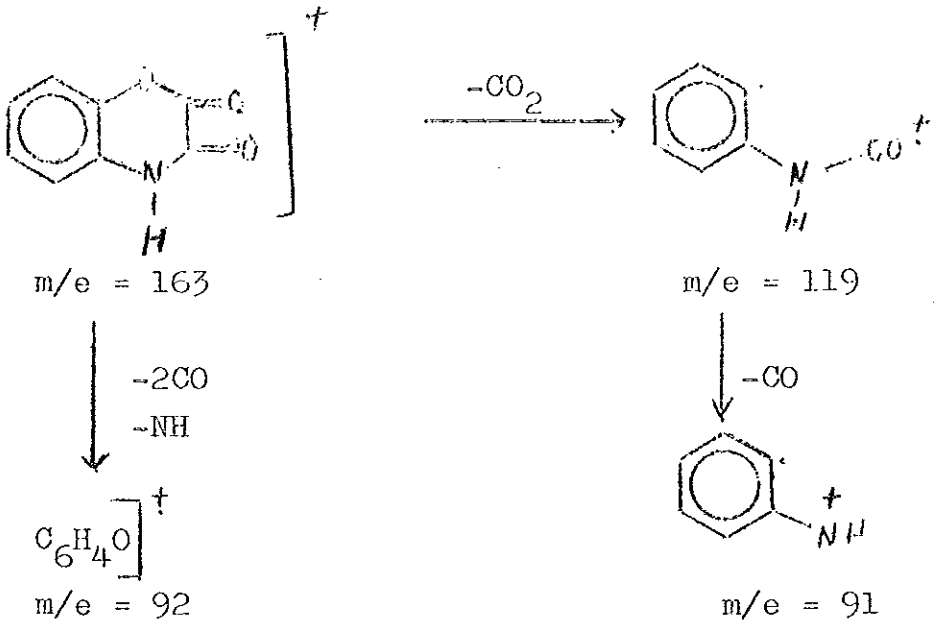


Fig. (14) Mass Spectra of compound BFB - 1

The reddish brown colour may be attributed to the presence of the two adjacent carbonyls in the benzoxazine system.

In an attempt to find more experimental evidence Bayer Villiger oxidation of isatin was done from which two products were obtained. One of them having the same R_f value as the compound RFB -(1). Rigorous characterization of the Bayer Villiger oxidation product was precluded by the inavailability of sufficient starting material.

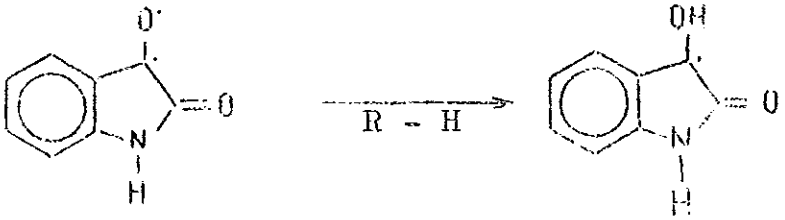
The intense fragments recorded in the mass spectra may be explained in the following way.



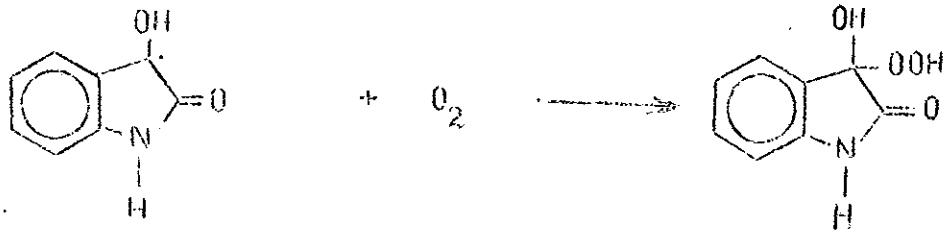
The proposed mechanism for this reaction is

1. Excitation step

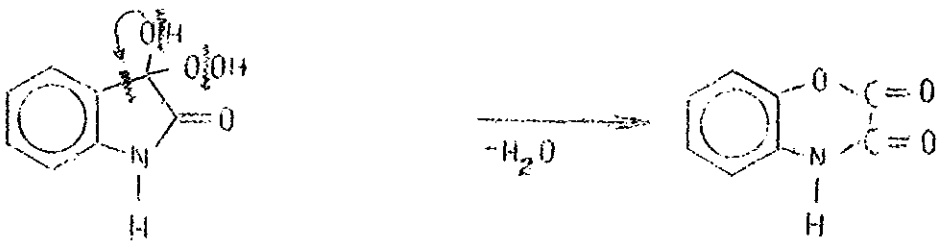
2. Abstraction of Hydrogen atom



3. Addition and hydrogen abstraction



4. Loss of water and α-cleavage



Compound - RFA - 2

A light yellow substance which forms 95% of the total product. It was recrystallized from acetone. The compound is insoluble in non-polar solvents like benzene, slightly solulbe in acetone and chloroform and soluble in highly polar solvent like DMSO. It has a melting point at 229 - 230°C.

Characterization of this compound was made mainly by spectroscopic means.

Identification

1. ^{13}C - NMR

All together eight carbon signals are observed

a) A carbonyl carbon at 175.86 ppm

b) Aromatic carbons 142.06, 128.06, 130.12 125,68, 121.21 and 109.13 ppm.

c) A quaternary carbon at 77.82 ppm (a signlet).

One can note that each peak in the ^{13}C-NMR appears as a doublet indicating the presence of isomeric compounds.

2. IR

The signal at 3200 cm^{-1} could be assigned to the NH streching with characteristic amide pattern seenin compounds like isoindigo (Fig.16). A signal at 740 cm^{-1} is due to N-H wagging and further evidence of the presence of the N-H group comes from the peak at 1470 cm^{-1} which is assigned to N-H bending vibrations. At 3330 cm^{-1}

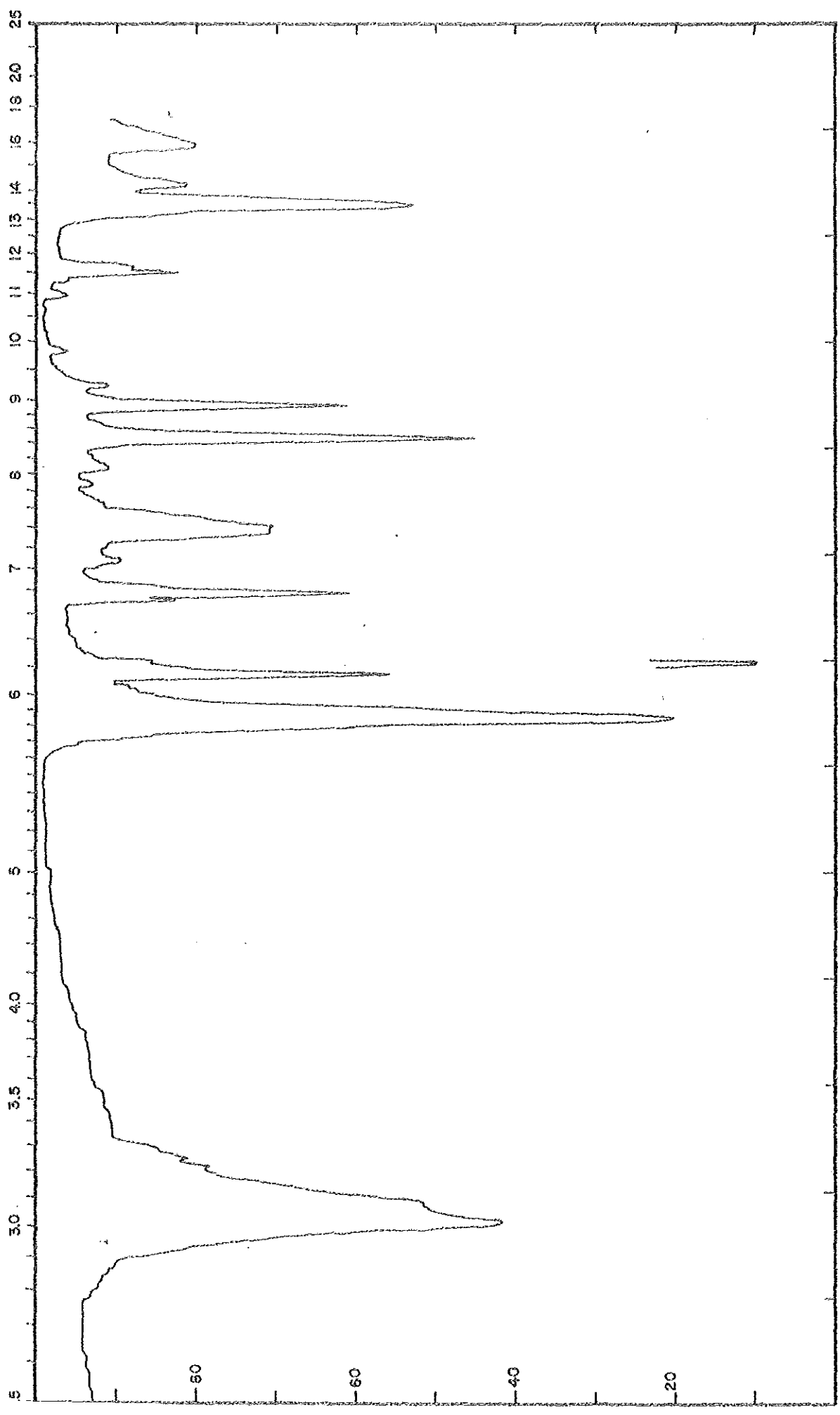


Fig. (15) IR SPECTRA RFA-2

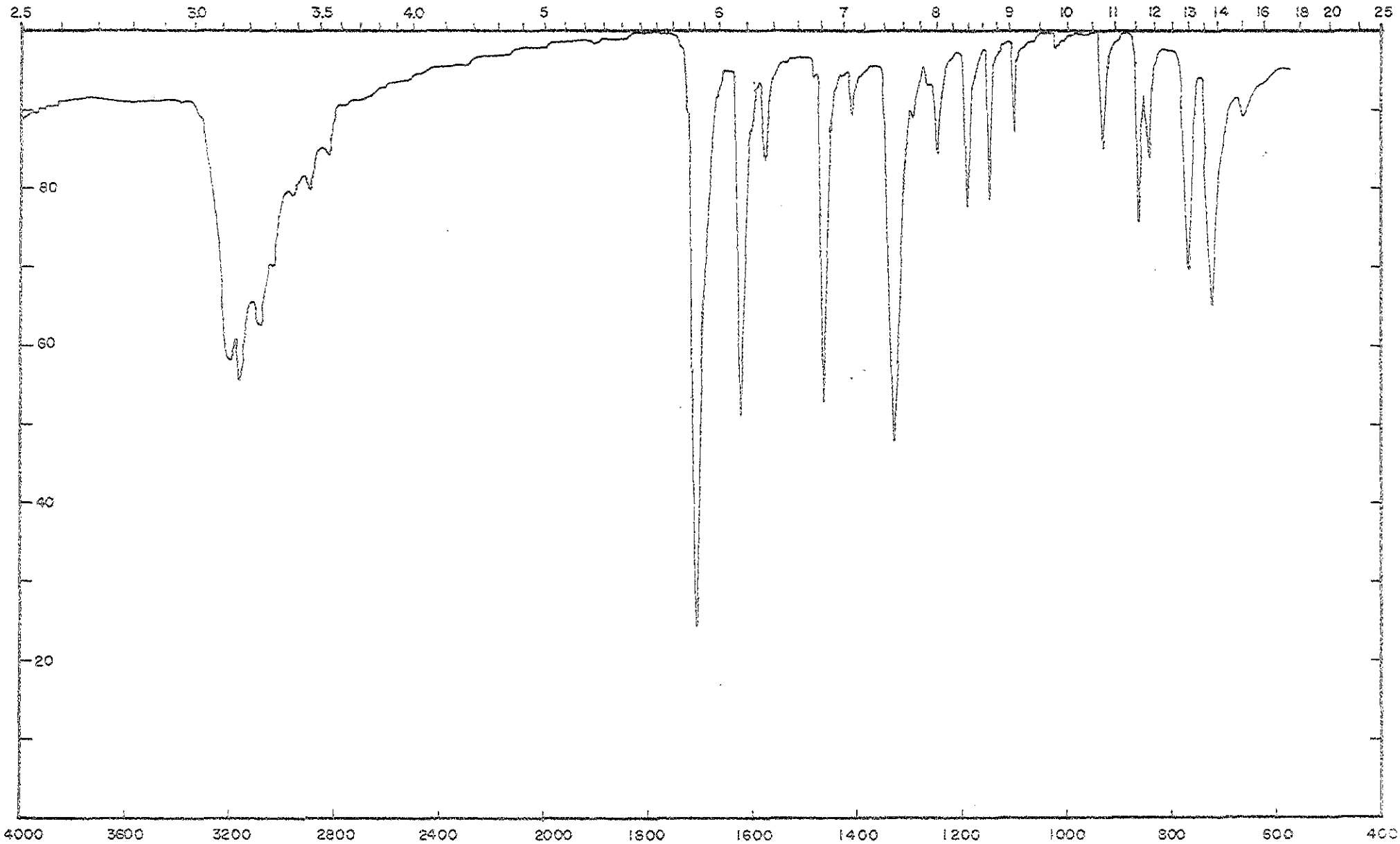


Fig. (16) IR Spectra of Isoindigo

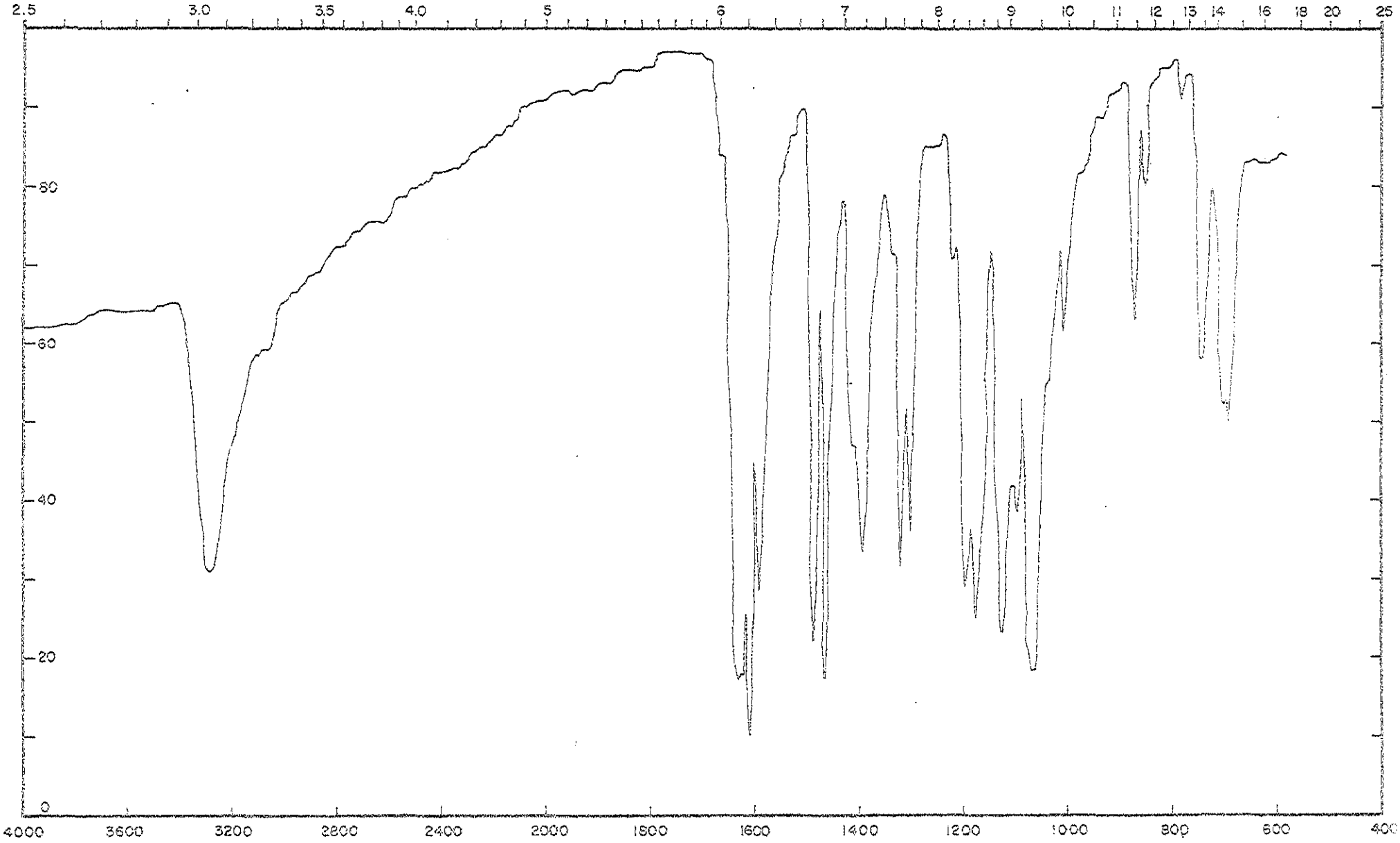


Fig. (17) IR Spectra of Indigo

overlapping with the amide N-H is a sharp signal assigned to an-OH streching vibrations.

In agreement with ^{13}C-NMR a band at 1710 cm^{-1} characteristic of an amide carbonyl group is assigned to C = O stretching. A further agreement with the ^{13}C-NMR comes from absorption at 1620 cm^{-1} and 1485 cm^{-1} which is characterstic of 1, 2 disubstituted benzene ring. The sharp absorption at 1340 cm^{-1} is assigned to C-N stretching vibrations. Finally the absorption at 1120 cm^{-1} is due to C-O stretching vibration.

3. ^{1}H-NMR

A broad peak at 4.3 ppm is assigned to N-H hydrogen. The presence of the N-H group has already been confirmed by IR.

The signal at δ =10.07 ppm is assigned to the hydroxyl hydrogen. T is was confirmed by the addition of D_2O where the signal for -OH roton disappeared and signal for a proton in H-OD appeared. Signals between δ = 6.0 ppm to δ =8.0 ppm are assigned to aromatic protons.

4. The Mass-spectra

The intense peak at m/e = 296 is assigned to the molecular ion peak. Other intense peaks in the spectrum are at m/e 149, 147, 119, 91 and 92.

In deducing the molecular structure of this compound it is important to remember the already established fact about

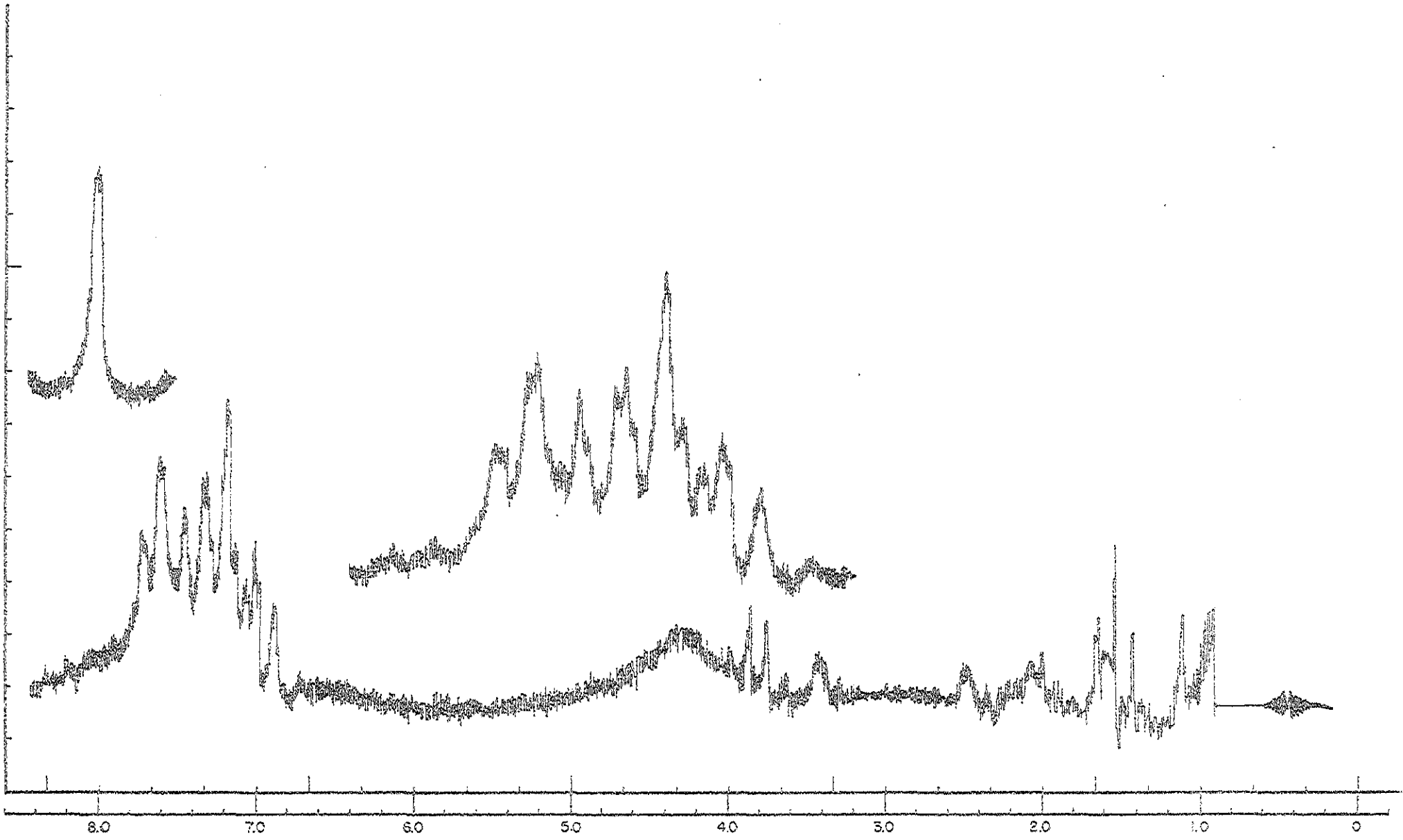


Fig. (18) H-NMR Spectra RFA-2 in DMSO

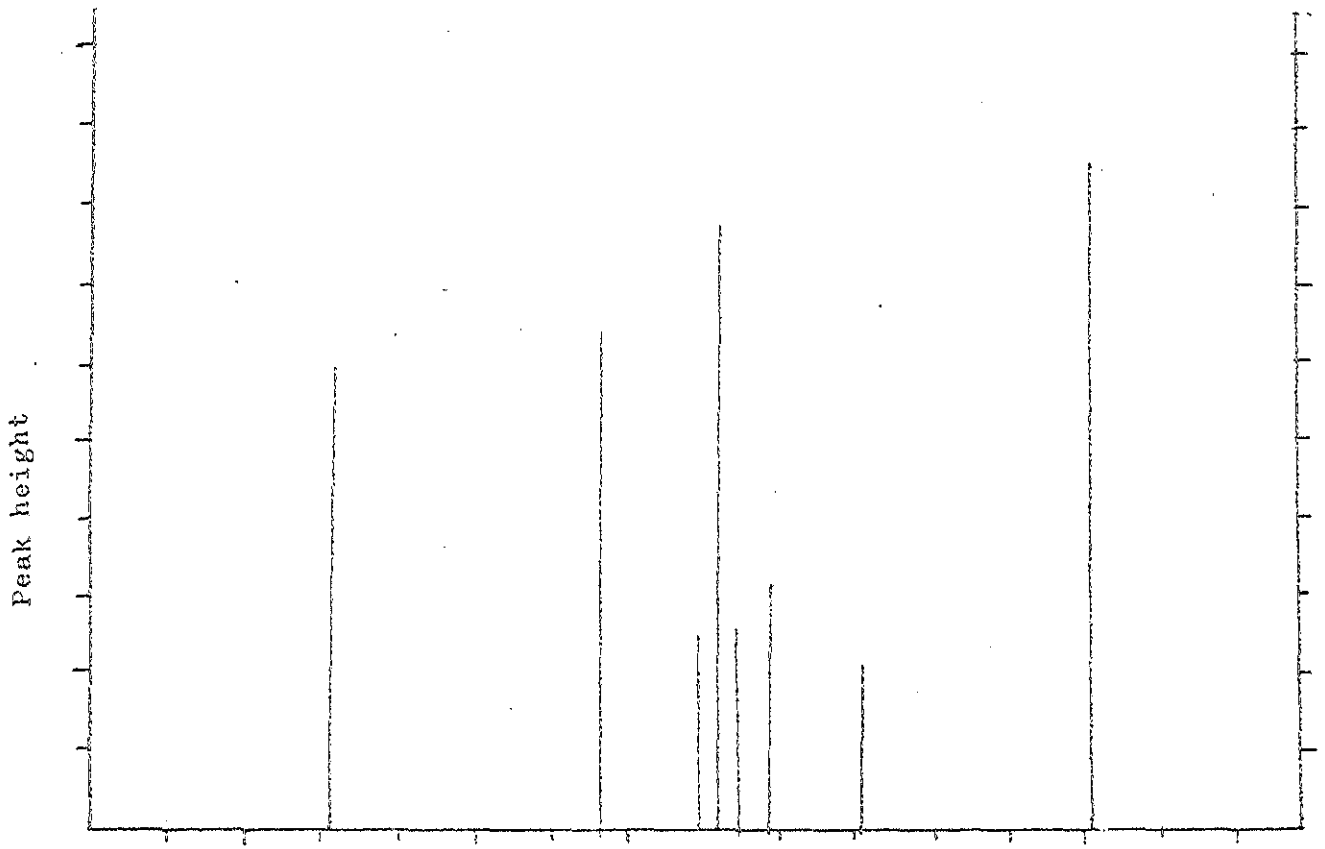


Fig. (19) ^{13}C - NMR Spectra RFA 2 in DMSO

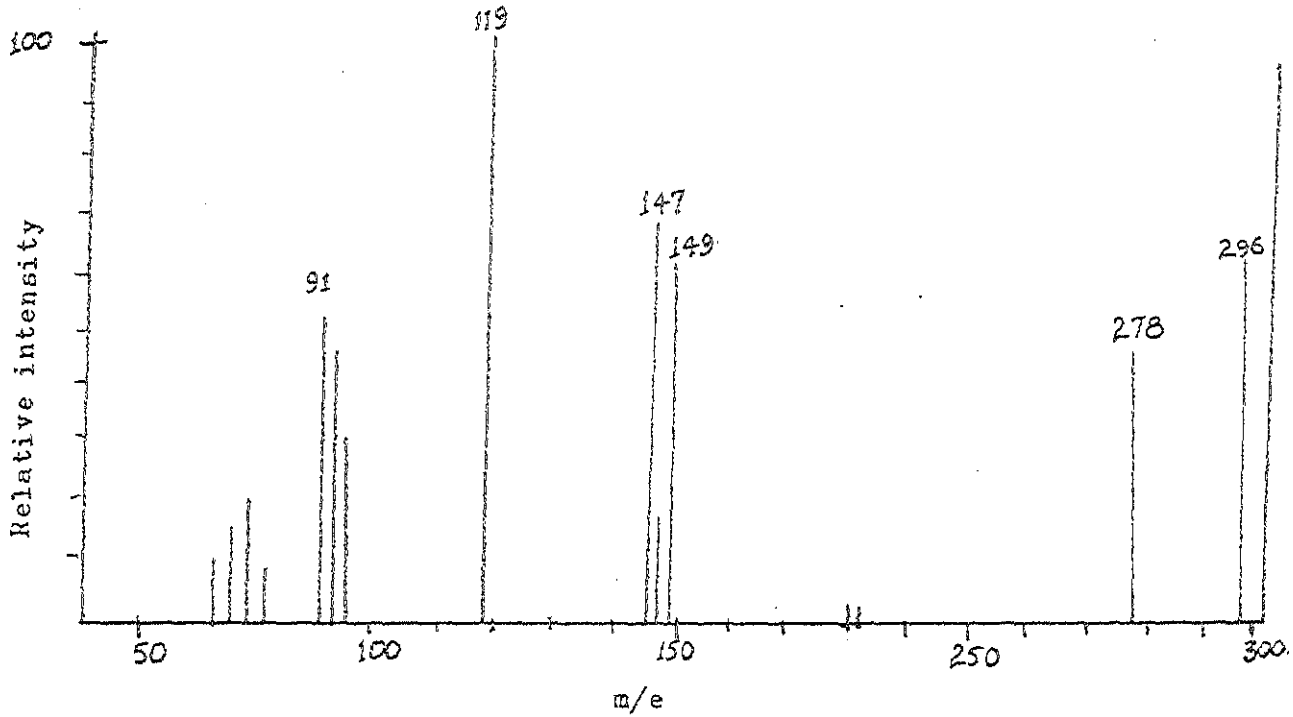
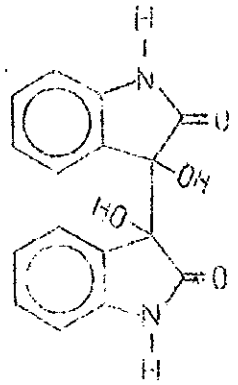


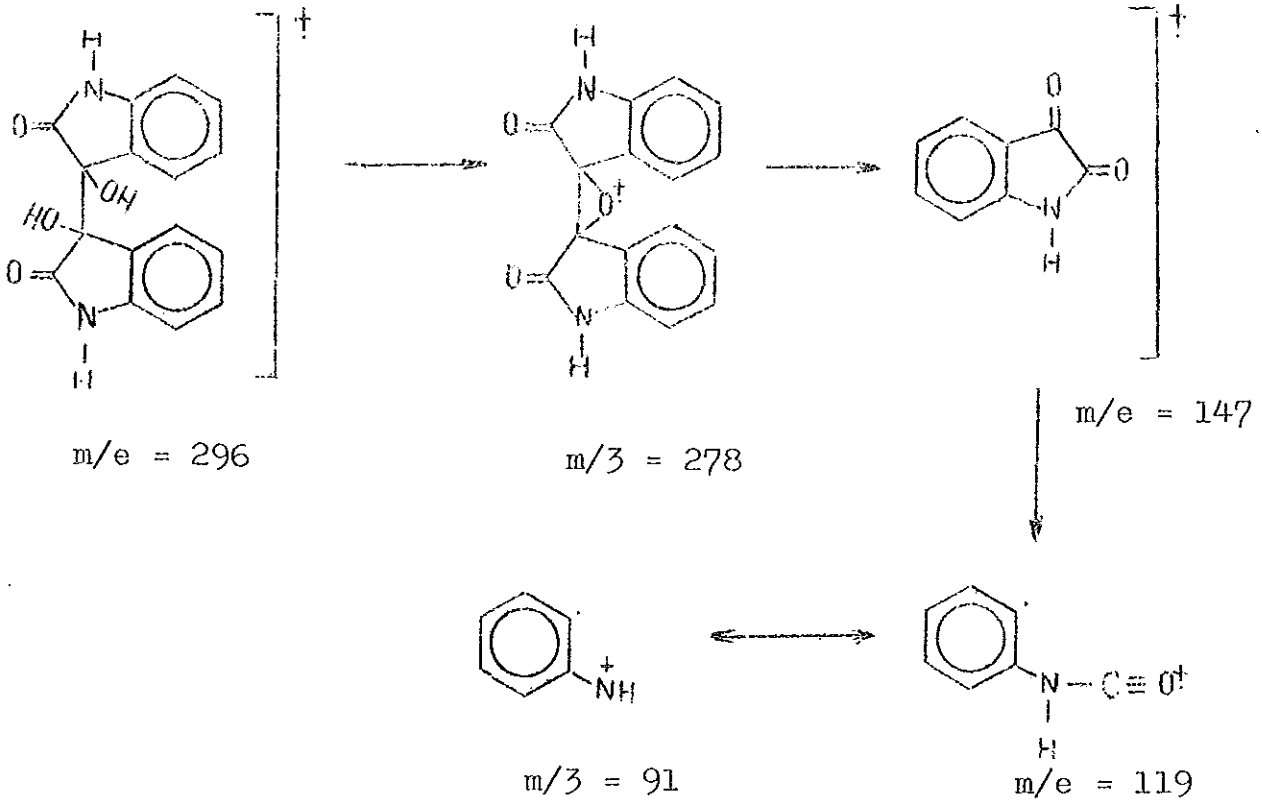
Fig. (20) Mass Spectra of RFA - 2

abstraction of hydrogen from the solvent by the isatin molecule. A structure in agreement with this and all the spectroscopic data is the following:



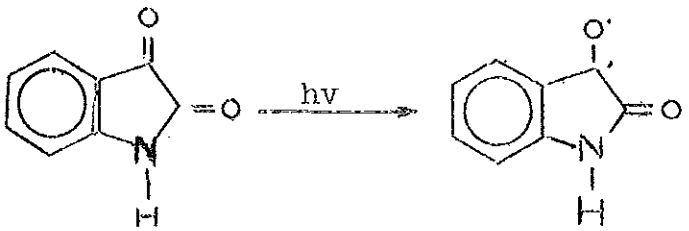
3,3' dihydroxy-3,3'-Bioxyindole

Additional experimental support to the formulation of this structure comes from oxidation of this compound (RFA-1) by paraiodic acid which gave a product with the same R_f values as an authetic isatin sample. From this structure the intense peaks in the mass spectrum can be expalined as follows:

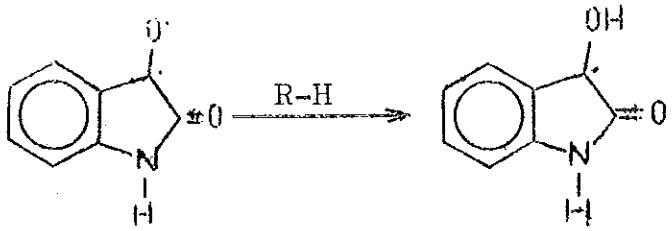


Reaction Mechanism:- from the studies with different solvents and spectral data the following mechanism is proposed.

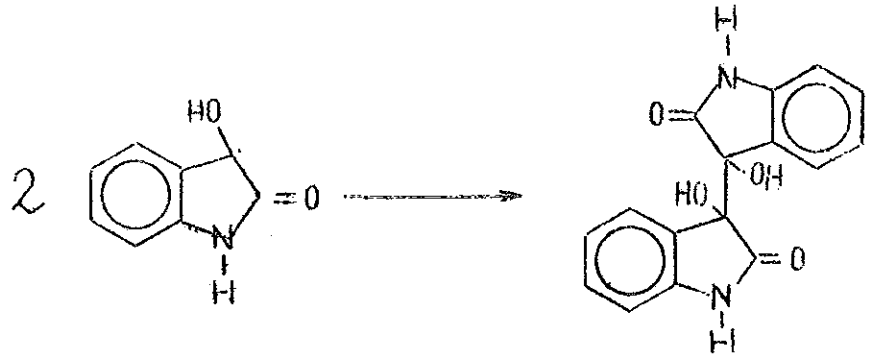
1. Excitation step



2. Abstraction of hydrogen atom by the excited carbonyl oxygen.



3. Dimerization



3,3' dihydroxy-3,3'Bioxyindole

Comparison λmax of isatin, RFA-1 and RFA-2 in methanol

Compound	max
Isatin	410 nm
RFB(2)	404 nm
RFA(1)	360 nm

Isatin and RFB(1) are α dicarbonyl compounds. The interaction of the two adjacent carbonyl groups (as has been demonstrated with the energy level diagram of isatin) will decrease the excitation energy and therefore increases the λ max. The effect of the electronegative oxygen atom in RFB(2) is to increase the excitation energy and therefore lower λ max compared to isatin. The compound RFA(1) possesses a much lower λmax. This is because it has only one carbonyl group and such an interaction is not possible.

5. The Reaction quantum yield

The efficiency of a chemical reaction can be expressed by the quantum yield (ϕ) which relates the effectiveness with which absorbed photons can form products i.e.

$$\Phi = \frac{\text{number of molecules decomposed or formed } S^{-1}\ cm^{-1}}{\text{number of quanta absorbed } S^{-1}\ cm^{-1}}$$

The reaction quantum yield could be roughly estimated in the following way:-

for the reaction

$$A \xrightarrow{h\nu} B$$

$$\frac{d c_A}{dt} = -\Phi_{A \rightarrow B} \; I_A, \text{abs}$$

where $\Phi_{A \rightarrow B}$ represents the photochemical quantum yield for the reaction $A \rightarrow B$.

and I_A, abs represents absorbed light intensity of A. With the presumption that at the excitation wavelength

$$A_B = 0 \quad \text{and} \quad A_A = 0.05$$

where A_A stands for absorbance of A

One can write

$$I_A, \text{abs} = I_O \; E'_A \; C_A l$$

E'_A = molar absorptivity at the excitation wavelength

Thus

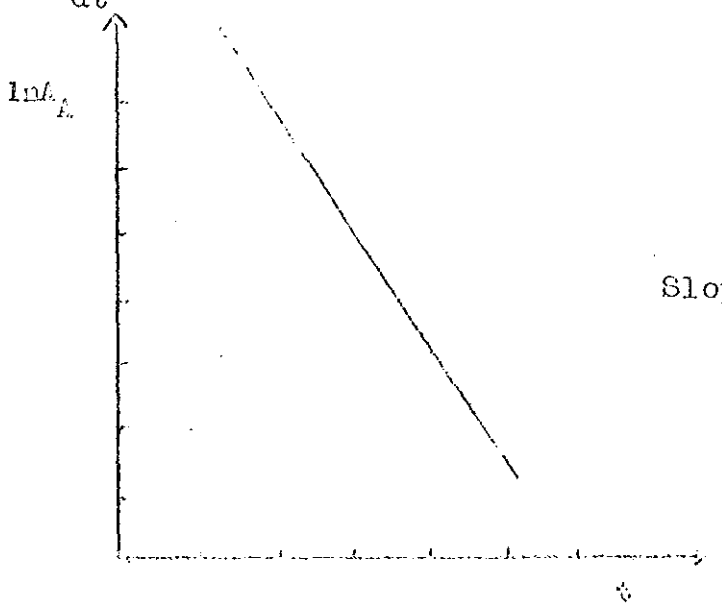
$$\frac{d c_A}{dt} = -\Phi_{A \rightarrow B} \; I_O \; E'_A \; C_A$$

substituting for $C_A = \frac{A_A}{E_A l}$

$$\frac{1}{E_A l} \quad \frac{d A_A}{dt} = -\Phi_{A \rightarrow B} \; I_o \; E'_A \; l \; \frac{A_A}{E_A l}$$

$$\frac{1}{A_A}\frac{dA_A}{dt} = -\phi_{A\rightarrow B} I_O E'_A l$$

$$\frac{d \ln A_A}{dt} = -\phi_{A\rightarrow B} I_O E'_A l$$



$$\text{Slope} = -\phi_{A\rightarrow B} I_O E'_A l$$

Thus, using a standard compound (actinometer) with known ϕ_{A-B} and E_A, and the same irradiation source (I_O) and the same cuvette (l), one can determine ϕ_{A-B} by comparison of the slopes (provided E'_A of the unknown sample is known).

The actinometer used in this work is the cis - trans isomerization reaction of N,N'-diacetyl indigo.

Both the actinometer and isatin were dissolved in cumene and purged with nitrogen gas. Irradiation

was done by high intensity monochromator at 436 nm. The progress of the reaction was followed by measuring the absorbance at different times. From the slope of the plot of ln A vs time and known quantum yield of the actinometer (0.03) the quantum yield of isatin has been estimated to be 0.03.

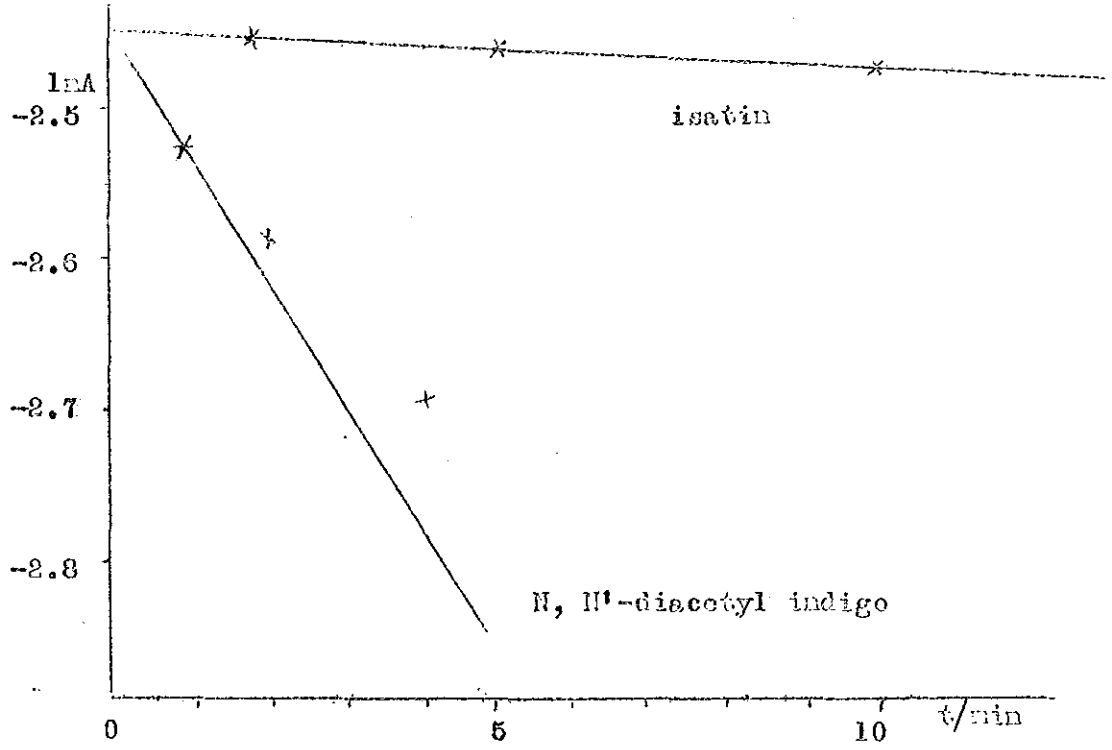


Fig. 21 Plot for ln A vs time for estimation of the reaction quantum yield

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