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The Photochemistry of Alpha, Beta-UnSaturated Nitro Compounds

Liang-Wuen Chang
Western Kentucky University

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Chang,
Liang-Wuen
1978
THE PHOTOCHEMISTRY OF ALPHA, BETA-UNSATURATED NITRO COMPOUNDS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Liang-Wuen Chang
May 1978
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THE PHOTOCHEMISTRY OF ALPHA, BETA-UNSATURATED NITRO COMPOUNDS

Recommended 22 May 1978

John W. Reasoner
Director of Thesis

John C. Craig Jr.

Curtis C. Wilkins

Approved June 7, 1978

Elmer Gray
Dean of the Graduate College
1-(9-Anthryl)-2-nitropropene and 1-(3-pyridyl)-2-nitropropene were prepared and irradiated with ultraviolet light.

Irradiation of 1-(9-anthryl)-2-nitropropene, in which the ethylene group was twisted out of the plane of the aromatic ring and the resonance stabilization between the ethylene group and the aromatic ring was limited, gave only cis-trans isomerization.

Irradiation of 1-(3-pyridyl)-2-nitropropene gave an oxime. The effect of added HCl on the reactivity of 1-(3-pyridyl)-2-nitropropene showed that the rate for the formation of oximinoketone was decreasing, while irradiation of 1-phenyl-2-nitropropene with HCl showed that the rate for the formation of oximinoketone was increasing.

From these observations, steric factors and resonance factors are postulated to have a rather large influence on the nitro-nitrite rearrangement and the extent to which it will occur.
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CHAPTER I

INTRODUCTION

The photochemical rearrangement of \(\beta\)-methyl-\(\beta\)-nitrostyrene to an \(\alpha\)-oximinoketone was first observed in 1964 by Chapman and co-workers.\(^1\) This unusual reaction which is different from previous observations of photodimerization\(^2\) and photoisomerization\(^3\) was attributed to the steric effect of the methyl group. The nitro group of the \(\alpha,\beta\)-unsaturated nitro compound was forced out of the plane of the aromatic ring to undergo a nitro-nitrite rearrangement.\(^1,4\)

In 1966 it was suggested that acetone might be playing an important role as a sensitizer in the rearrangement.\(^4\) The solvent effect on the photorearrangement was investigated by Chen\(^5\), indicating that acetone is not a necessary sensitizer for the reaction since other aqueous solvents also gave high yields of \(\alpha\)-oximinoketone.

From 1973 to 1975 a series of substituent effects on the aromatic ring of the \(\alpha,\beta\)-unsaturated nitro group were reported by Pinhey and Rizzardo\(^6\), by Tang\(^7\), by Matsurra et al.\(^8\), and by Kassaee\(^9\). The electron withdrawing groups at the \textit{para} and the \textit{meta} position of the aromatic ring inhibited the formation of the \(\alpha\)-oximinoketone and promoted cleavage of the styrene derivative. The electron donating groups at the \textit{ortho} position of the aromatic ring promoted the formation of \(\alpha\)-oximinoketone.

Elomore\(^10\) reported that the steric hindrance from a \textit{peri} and \textit{ortho} hydrogens of 1-(1-naphthyl)-2-nitropropene and two methyl groups of
1-(2,4,6-trimethylphenyl)-2-nitropropene inhibited photochemical rearrangement to an oximinoketone. The steric hindrance forces the ethylene group out of the plane of the aromatic ring reducing the resonance interaction between the aromatic ring and the ethylene group.

The purpose of this study was to further investigate the steric inhibition of the photorearrangement, to prepare heteroaromatic α,β-unsaturated nitro compounds, and to investigate the resonance effect on the photorearrangement.
Trotter found that the dipole moments of conjugated aromatic nitro compounds, such as nitrobenzene (I) (3.95 Debye), are larger than those of the corresponding aliphatic nitro compounds (3.3 Debye). The increased dipole moments are due to contributions from ionic structures (II and III) which are maximum when the nitro group is coplanar with the aromatic ring.

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} \\
\text{(III)} & \quad \text{(IV)}
\end{align*}
\]

The introduction of methyl groups ortho to the nitro group, as in nitromesitylene (IV), reduces the dipole moment to 3.65 Debye, suggesting that the nitro group is twisted out of the plane of the benzene nucleus, and the contributions of structures II and III are reduced. The X-ray investigation (Table I) also confirmed that the nitro group is forced out of the plane of the benzene ring by adjacent group.
TABLE I

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>NO₂ TWIST (IN DEGREES)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-conjugated</td>
<td>90.0</td>
</tr>
<tr>
<td>9-Nitroanthracene</td>
<td>84.7</td>
</tr>
<tr>
<td>Nitromesitylene</td>
<td>66.4</td>
</tr>
<tr>
<td>9,10-Dinitroanthracene</td>
<td>63.7</td>
</tr>
<tr>
<td>Conjugated</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Kituara and Matsuura\textsuperscript{12} studied the \textit{aci}-nitro tautomer of 2,4,6-trimethylnitrobenzene (VII), 2,4,6-triethylnitrobenzene (IX) and 2,4,6-tributylnitrobenzene (X) in dioxane-deuterium oxide compared with the \textit{aci}-nitro tautomer of o-nitrotoluene (V)\textsuperscript{13}. The compounds IX and X failed to produce the corresponding \textit{aci}-nitro tautomer, which is due to the sterically hindered environment. Compound VII which is more hindered than compound V shows more difficult to undergo intramolecular hydrogen abstraction to produce the corresponding \textit{aci}-nitro tautomer (VIII) than compound V.

\[
\begin{align*}
\text{(V)} & \quad \text{(VI)} \\
\text{(VII)} & \quad \text{(VIII)}
\end{align*}
\]
In view of the sterically hindered nature, the 3,5-dimethyl-4-nitropyridine-1-oxide (XI) was studied by Kaneko et al. The irradiation of XI in ethanol or in isopropanol, either in the presence or absence of oxygen, resulted in the formation of 3,5-dimethyl-4-nitropyridine-1-oxide and its methyl substituted derivatives (XIV), in the same solvents, under the nitrogen flush, resulted in the formation of 4-hydroxyaminopyridine-1-oxide (XV) in a quantitative yield.
In XI the nitro group was believed to be forced out of the plane of the pyridine ring by the two methyl groups. The formation of an n,π excited species is facilitated to form intermediate XIII by the steric features. This is similar to that postulated in the rearrangement of γ-methyl-β-nitrostyrene.\textsuperscript{1,4}

In 1964 Chapman and co-workers\textsuperscript{1} found that the irradiation of γ-methyl-β-nitrostyrene (XVI) in either styrene or tetramethylethylene gave the α-oximinoketone (XVII). In contrast, the irradiation of γ-nitrostyrene (XVIII) in cyclohexene solution (XIX) gave photoaddition product (XX).

\[
\text{Ph-CH=CH-CH\textsubscript{3}NO\textsubscript{2}} \xrightarrow{\text{hv}} \text{Ph-C-C\textsubscript{3}H\textsubscript{3}} \text{NOH} \tag{XVI}
\]

\[
\text{Ph-CH=CH-H} \xrightarrow{\text{hv}} \text{Ph-C-cyclohexene} \xrightarrow{\text{hv}} \text{Ph-NO\textsubscript{2}} \tag{XX}
\]

Irradiation of 2,3-dimethyl-1-nitronaphthalene (XXI) in solution (acetone or 95% ethanol) gave 2,3-dimethyl-1,4-naphthoquinone (XXII) and other products.
For detailed investigation, 9-nitroanthracene (XXIII) and 6-nitrocholesta-3,5-diene (XXVII) were chosen by Chapman and co-workers\textsuperscript{16}. The irradiation of XXIII with continuous nitrogen flush gave anthraquinone (XXIV, 13%), 10,10'-bianthrone (XXV, 48%), anthraquinone mono-oxime (XXVI, 30%) and nitrogen oxide. Irradiation of XXVII in acetone under nitrogen flush produced 3-oximinocholest-4-en-6-one (XXVIII).

\[
\begin{align*}
\text{NO}_2 \quad \text{hv} \quad \text{N}_2 & \quad \rightarrow \quad \text{O} \quad \text{O} \\
\text{(XXIII)} & \quad \text{(XXIV)} + \text{(XXV)} \\
+ \quad \text{NOH} & \quad \text{NO} \\
\text{(XXVI)} & \quad \text{(XXVIII)}
\end{align*}
\]

A common feature which each of the four compounds undergoes during the rearrangement is an arrangement of atoms which keeps the plane of the nitro group out of the plane of the adjacent aromatic ring or double bond.
In 9-nitroanthracene (XXIII) this is achieved by two peri-hydrogens, in 1-nitro-2,3-dimethylnaphthalene (XXI) by a peri-hydrogen and o-methyl group, in 6-nitro-$\Delta^{3,5}$-cholestadiene (XXVII) by a C-4 hydrogen, while $\beta$-methyl-$\beta$-nitrostyrene was assumed to react via the isomer in which nitro and phenyl are cis (XVI). The following mechanism was postulated by Chapman and co-workers. The plane of nitro group is almost at right angles ($85^\circ$ in crystal) to the plane of the anthracene ring, and the nitro group may be regarded as essentially nonconjugated. The rearrangement was described in terms of an $n,\pi^*$ excited state. The overlap of the half-vacant nonbonding orbital of the nitro group with the adjacent orbital of the aromatic ring results in the formation of an oxaziridine ring.
Irradiation of 6-nitrocholesteryl acetate (XXXI) was investigated in different solvents, and solvent dependent products were reported. Pinhey and Rizzardo\textsuperscript{17} reported that irradiation of XXXI in hexane or aqueous dioxane did not give any oxime product, however, Chapman and co-workers\textsuperscript{16} found that irradiation of XXXI in acetone gave oxime and other products. It was postulated that acetone might be acting as a sensitizer for the photochemical nitro-nitrite rearrangement. Reid and co-workers\textsuperscript{18} reported that irradiation of XXXI in ethanol produced oxime which indicated that the presence of a sensitizer was not essential for the formation of oxime. Chen’s work on the solvent effects of \( \alpha,\beta \)-unsaturated nitro styrene indicated that acetone was not a necessary sensitizer for nitro-nitrite rearrangement while water played an important role in promoting the reaction.
Reid and co-workers attempted to rationalize the behavior of non-aromatic nitroalkenes. Irradiation of 1-cyclohexyl-2-nitroprop-1-ene (XXXVI) through a pyrex filter in the solvents, acetone, 1-propanol or cyclohexane gave nitroalkene (XXXVII, 50%-55%) and cyclohexylidene acetone (XXXVIII, 5%-25%). The unsaturated ketone was presumably formed via nitro-nitrite rearrangement. The formation of the unsaturated nitro compound is best interpreted as involving intramolecular γ-hydrogen abstraction in the cis-isomer (XXXIX), followed by rearrangement of the aci-nitro isomer (XL) to the nitroalkene (XXXVII).

\[
\begin{align*}
\text{XXXVI} & \quad \text{XXXVII} \\
\text{XXXIX} & \quad \text{XL} \\
\text{XXXVIII} & \quad \text{XXXVII}
\end{align*}
\]

In the irradiation of 6-nitrocholest-5-ene (XLI) in acetone or cyclohexane, a hydrogen atom is favorably positioned for abstraction via a six-membered transition state. A 45% yield of the nitroalkene (XLII) and a 20% yield of the ketone (VIII) was observed. An analogous reaction was observed in 4-nitrocholest-4-ene.
Irradiation of 3-nitrocholest-2-ene and 1-nitrocyclohexene (XLIV), which do not have γ-hydrogen atoms readily available for intramolecular abstraction, behaves quite differently on irradiation.

Pinhey and Rizzado⁶ found that cis-α-4-dinitrostilbene (XLVIII) was converted into 2-phenyl-2-hydroxyimino-4-nitroacetophenone (XLIX, 38%), bezaldehyde (L, 19%) and other products which were not indentified.
In order to study the electronic effect, a series of substituents on the aromatic ring of \( \alpha,\beta \)-unsaturated nitro compounds were investigated by Matsurra and co-workers\(^8\), by Tang\(^7\) and by Kassaee\(^9\). Electron withdrawing groups on the aromatic ring tend to favour a cleavage reaction (path a) by forming an aldehyde. Electron donating groups on the aromatic ring tend to favour the nitro-nitrite rearrangement (path b). Kassaee included the ideas of Chapman\(^1\), Pinhey\(^6\) and Matsurra\(^6\) and proposed two path-ways for the formation of the different products.
Matsurra examined the quenching effect of piperlene and indicated that path a proceeds via the lowest triplet state and path b proceeds via a singlet or a higher triplet state T2. In order to compare nitro n-\pi* photochemistry with carbonyl n-\pi* reactivity, 3,3-diphenyl-1-nitrocyclohexane (LIV) and 4,4-diphenylcyclohexenone (LV) were selected by Zimmerman21 for photochemical study. The n-\pi* triplet was proposed as the excited state.
Crosby\textsuperscript{21} found E-1-(9-phenanthryl)-2-nitroprop-1-ene (LVI) on irradiation in dioxane or sensitization with camphorquinone gives the Z isomer which is photochemically reactive and produces phenanthrene-9-carboxaldehyde (LVII, 25\%) and the furan derivative (LVIII, 5\%). The mechanism of product formation has been explored.
According to the report of Pinhey, the intramolecular cycloaddition of a nitro group to a carbon-carbon double bond has been suggested for the photochemical double bond cleavage of cis-α-4-nitrostilbene. Comparing this with the report of Crosby that the Z isomer is photochemically reactive; the reaction still remains ambiguous and needs to be clarified.

Substituents other than the methyl on the β-position of β-nitrostyrene compounds and on the ortho position of the aromatic ring of β-nitrostyrene compounds were studied by Elmore. He found that the rate of rearrangement using large groups on the β-position of β-nitrostyrene does not show a noticeable change, but the bulky group on the ortho position of the aromatic ring causes the ethylene group to twist out of the plane of the aromatic ring. No oxime was found in the irradiation of 1-(2,4,6-trimethylphenyl)-2-nitropropene (LX), and 1-(1-naphthyl)-2-nitropropene (LXI), whereas 1-(2-naphthyl)-2-nitropropene (LXII) shows a greater reaction rate compared to the 1-phenyl-2-nitropropene to form the corresponding α-oximinoketone.

\[
\begin{align*}
(LX) & \quad (LXI) & \quad (LXII)
\end{align*}
\]
CHAPTER III
EXPERIMENTAL

I. Instrumentation

N.M.R. spectra were recorded on a Varian A 60D 60 MHz instrument. Infrared spectra were recorded on Perkin-Elmer Model 710 spectrophotometer. Solid samples were run in NUJOL or KBr pellet. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. Mass spectra were obtained courtesy of the University of Kentucky, Lexington. Melting points were done on a Fisher-Jones melting point apparatus and were reported as uncorrected. Gas chromatography was carried out on a Varian Model 1720 dual column instrument with disc integrator and temperature programming capability.

III. Irradiation Apparatus

A Hanovia type A-36 550-watt medium pressure mercury arc lamp was used as the light source. The lamp was inserted into the immersion well of a jacketed pyrex tube. The pyrex tube was equipped with a 60/50 standard taper joint which had been wrapped with teflon tape. The tube was fitted into a 550 ml. capacity reaction vessel containing three side-arm exists near the top to accommodate a thermometer, gas dispersion tube, and a condenser when necessary.

When the irradiation was carried out, nitrogen gas was bubbled through the solution for one-half hour prior to irradiation and continuously during the irradiation. The temperature of the solution was monitored
during each irradiation using water flow through the cooling jacket to keep the temperature of the solution below 35°C.

The kinetic study was carried out by taking aliquots at certain time intervals and the solution for u.v./vis. spectra was prepared by diluting 1 ml. of aliquot to 100 ml. or other suitable concentration. The wavelengths for u.v. study were selected between 400 nm to 200 nm. For visible study wavelengths between 650 nm to 300 nm were selected.

III. Gas Chromatography

Irradiation products were analyzed on Varian Model 1720 dual column gas chromatography.

A 6 foot 10% FFAP column was used for the gas chromatography analysis. With this column instrument settings were as follows: detector temperature 300°C; injection temperature 275°C; oven temperature 160°C; filament current 150 milliamps; average helium flow rate 75 ml./min.; attenuation x1.

The yield of the rearrangement product was obtained by the method of Rosie and Grob²². An internal standard was chosen with a retention time different from starting material and irradiation product. A solution containing an X:1 mole ratio (X=1, 2, 3) of irradiation product to internal standard was prepared using ethanol as solvent. 1 to 2 μl. of this solution was injected into the gas chromatograph and the relative response factor was obtained by calculating the number of counts of irradiation product to internal standard from the disc integrator. After the α,β-unsaturated nitro compound was irradiated, the internal standard with the same molar ratio as the relative response factor was added into the irradiated mixture. The solution was concentrated by using reduced
pressure, and then a small amount of ethanol was added to dissolve the mixture. A ratio of irradiation product count to internal standard count was calculated and divided by the relative response factor to give the molar percent of irradiation product formed.

IV. Preparation of α,β- Unsaturated Nitro Derivatives

(A) Synthesis of 1-(9-anthryl)-2-nitropropene

The method of Robertson \(^{23}\) was used to prepare 1-(9-anthryl)-2-nitropropene. 9-Anthraldehyde (0.1 mole) was dissolved in 50 ml. of benzene and n-butylamine (0.1 mole) was added to the solution. The mixture was refluxed for one and one-half hours until the theoretical amount of water (1.8 ml.) was collected in the modified Dean and Stark moisture trap.

Then the benzene solution was removed by using vacuum distillation, and the crude Schiff’s base was obtained. Another solution of 7.5 g. of nitroethane (0.1 mole) in 25 ml. of acetic acid was prepared and added to the crude Schiff’s base. The mixture was allowed to stand at room temperature for five days. Crystals were collected and washed with a small amount of cold water. The product was recrystallized from acetone three times to yield 20 g. of orange crystals with a melting point of 145-146° C.

The infrared spectrum showed prominent peaks at 1510, 1440, 1380, 1320, 960, 895, and 820 cm\(^{-1}\) The mass spectrum showed a parent peak at 263 with other fragments at 246, 233, 217, 216, 215, 202, 178, and 177. The structure of 1-(9-anthryl)-2-nitropropene was in agreement with these spectra.

(B) Synthesis of 1-(3-pyridyl)-2-nitropropene

The method of Burgen, Strin, and Clements \(^{24}\) was used to prepare 1-(3-pyridyl)-2-nitropropene. A mixture of 5.35 g. (0.005 mole) of pyridine-
3-aldehyde, 3.75 g. (0.005 mole) nitroethane and 8-10 drops of n-butylamine in a 100 ml. round bottom flask was refluxed for 3 hours. The solution was cooled with ice and allowed to stand and the crystals to form. The crystals were filtered and washed with petroleum ether. Recrystallization from a small amount of ethyl acetate or from ligroin gave 4.2 g. (51%) of yellow prisms, m.p. 67-68°C (reported 67.5-68°C). The infrared spectrum showed prominent peaks at 1670, 1600, 1520, 1420, 1325, 1260, 980, 865, and 700 cm.\(^{-1}\) The mass spectrum showed a parent peak at 164 with other fragments at 147, 134, 118, 117, 106, 91, 90, and 78 m/e. The structure of 1-(3-pyridyl)-2-nitropropene was in agreement with these spectra.

V. Photochemical Synthesis of Keto Oxime

(A) Irradiation of 1-(9-anthryl)-2-nitropropene

1-(9-Anthryl)-2-nitropropene (1 g.) was dissolved in 400 ml. of 95% undenatured ethanol and the solution was degassed with nitrogen for one-half hour. The irradiation was carried out for two hours with u.v. light and nitrogen gas bubbled through the solution during the irradiation. The solution temperature was maintained below 35°C with water flow through the cooling jacket.

The solvent was concentrated by vacuum distillation down to about 20 ml. total volume. The t.l.c. showed two components; one being starting material and the other being photoproduct. The separation of the two components was carried out by using column chromatography which was packed with silica gel (60/80 mesh) and eluted with carbon tetrachloride. The solvent was removed under reduced pressure and 0.4 g. of starting material and 0.3 g. of methyl hydrogen trans photoproduct was obtained with the melting point of 99-101°C. The mass spectrum when compared with starting material showed identical peaks. The I.R. spectrum showed the predominate
peaks shifted to higher frequency than the starting material at 1625, 1450, 1390, 1340, and 890 cm\(^{-1}\). The N.M.R. peak showed splitting of the -CH\(_3\) peak at \(\delta = 2.4\). The structure of 1-(9-anthryl)-2-nitropropene was assigned the methyl hydrogen trans isomer.

(B) Synthesis of 1-(3-pyridyl)-1,2-propanedione-1-oxime

1-(3-Pyridyl)-2-nitropropene (2.0 g.) was dissolved in 400 ml. of 95% undenatured ethanol and the solution was degassed with nitrogen for one-half hour. The irradiation was carried out for two hours with u.v. light and nitrogen gas was bubbled continuously through the solution during the irradiation interval. The temperature of the solution was kept below 35° C with water through the cooling jacket.

The solvent was removed by vacuum distillation down to about 20 ml. total volume and cooled with ice to allow the crystals to form. After the solid was filtered and washed with ethanol, the solid was recrystallized from 95% undenatured ethanol. A white solid (0.7 g.) was collected and found to have melting point of 210-211° C. The I.R. spectrum of this white solid showed prominent peaks at 1680, 1675, 1600, 1580, 1300, 1195, and 1010 cm\(^{-1}\). In contrast, the peaks of starting material showed the presence of the -C=O peak and the absence of the -NO\(_2\) peak. The mass spectrum showed a parent peak at 164 with other fragments at 149, 147, 121, 105, 104, 78, 43, 28, and 20 m/e. The structure of 1-(3-pyridyl)-1,2-propanedione-1-oxime was in agreement with these spectra.

VI. The Kinetic Study of the Photochemistry of \(\alpha,\beta\)-unsaturated Nitro Compounds under \(\text{N}_2\)

(A) Photochemical Isomerization of 1-(9-anthryl)-2-nitropropene

A 0.0002 mole (0.0526 g.) sample of 1-(9-anthryl)-2-nitropropene was dissolved in 95% undenatured ethanol. The solution was degassed with \(\text{N}_2\)
for one-half hour and irradiated under continuous N\textsubscript{2} flush. A two ml. aliquot sample was withdrawn after 0, 5, 10, 15, 30, 60, 90, and 120 minutes. A 1 ml. portion of the aliquot sample, which was scanned in the u.v. region, was diluted by adding 75 ml. of 95\% undenatured ethanol. Another 1 ml. of aliquot sample, which was scanned in the visible region, was diluted by adding 5 ml. of 95\% undenatured ethanol. The solution showed that the absorption bands shifted to shorter wavelength from 0 time to 120 minutes in the visible region and shifted to longer wavelength from 0 time to 120 minutes in the u.v. region.

(B) Photochemical Rearrangement of 1-(3-pyridyl)-2-nitropropene

A solution of 0.0035 mole (0.57 g) of 1-(3-pyridyl)-2-nitropropene was dissolved in 95\% undenatured ethanol. The solution was degassed with nitrogen for one-half hour and irradiated under continuous nitrogen flush. A 1 ml. aliquot sample was withdrawn after 0, 5, 10, 15, 30, 60, 90, and 120 minutes, and each sample was diluted to 100 ml. with 95\% undenatured ethanol. The ultraviolet spectra of these solutions showed the absorption at 292 nm to be decreasing on continuous irradiation. A rate constant \((1.796 \times 10^{-2}\text{min}^{-1})\) was obtained from the slope of a first order plot of \(-\log(\text{Absorbance})\) vs Time. The half-life was calculated to be 38.6 minutes.

(C) Photochemical Rearrangement of 1-(3-pyridyl)-2-nitropropene containing an equal molar amount of hydrochloric acid

A solution of 0.0035 mole (0.57 g) of 1-(3-pyridyl)-2-nitropropene and 0.0035 mole (0.34 g) of HCl (37.4\%) was prepared in 400 ml. of 95\% undenatured ethanol. The solution was degassed with nitrogen for one-half hour and irradiated under nitrogen flush. A 1 ml. aliquot sample was withdrawn after 0, 5, 15, 30, 60 90, and 120 minutes and each sample was diluted to 100 ml. with 95\% undenatured ethanol. The ultraviolet spectra
of these solutions showed a decrease in the absorption at 292 nm. A rate constant \((1.368 \times 10^{-2}\text{ min}^{-1})\) was obtained from the slope of a first order plot of \(-\log(\text{Absorbance})\) vs Time. The half-life was calculated to be 50.62 minutes.

(D) Photochemical Rearrangement of 1-(3-pyridyl)-2-nitropropene containing a five-fold excess of hydrochloric acid

A solution of 0.0035 mole (0.57 g) of 1-(3-pyridyl)-2-nitropropene and 0.0175 mole (1.7 g) of HCl (37.4%) was prepared in 400 ml. of 95% undenatured ethanol. The solution was degassed with nitrogen for one-half hour and irradiated under nitrogen flush. A 1 ml. aliquot sample was withdrawn after 0, 5, 10, 15, 30, 60, 90, and 120 minutes and each sample was diluted to 100 ml. with 95% undenatured ethanol. The ultraviolet spectra of these solutions showed the disappearance of the absorption at 292 nm. A rate constant \((7.25 \times 10^{-3}\text{ min}^{-1})\) was obtained from the slope of a first order plot of \(-\log(\text{Absorbance})\) vs Time. The half-life was calculated to be 95.5 minutes.

(E) Photochemical Rearrangement of 1-(1-pyridyl)-2-nitropropene containing a ten-fold excess of hydrochloric acid

A solution of 0.0035 mole (0.57 g) of 1-(3-pyridyl)-2-nitropropene and 0.0035 mole (3.4 g) of HCl (37.4%) was prepared in 400 ml. of 95% undenatured ethanol. The solution was degassed with nitrogen for one-half hour and irradiated under nitrogen flush. A 1 ml. aliquot sample was withdrawn after 0, 5, 10, 15, 30, 60, 90, and 120 minutes and each sample was diluted to 100 ml. with 95% undenatured ethanol. The ultraviolet spectra of these solutions showed the decrease in the absorption band at 292 nm. A rate constant \((6.93 \times 10^{-3})\) was obtained from the slope of a first order plot of \(-\log(\text{Absorbance})\) vs Time. The half-life was calculated to be 100 minutes.
The photochemical rearrangement of 1-phenyl-2-nitropropene containing a five-fold excess of hydrochloric acid

A solution of 0.0035 mole (0.57 g) of 1-phenyl-2-nitropropene and 0.0175 mole (1.7 g) of HCl (37.4%) was prepared in 400 ml. of 95% undenatured ethanol. The solution was degassed with nitrogen for one-half hour and irradiated under nitrogen flush. A 1 ml. aliquot sample was withdrawn after 0, 5, 10, 15, 30, 60, 90, and 120 minutes, and each sample was diluted to 100 ml. with 95% undenatured ethanol. The ultraviolet spectra of this solutions showed a decrease in the absorption at 305 nm. A rate constant (9.12 x 10^{-2}) was obtained from the slope of a first order plot of $-\log$ (Absorbance) vs Time. The half-life was calculated to be 7.5 minutes.

VI. Photochemistry and Gas Chromatography Measurement of $\alpha,\beta$-Unsaturated Nitro Compounds

A 10% FFAP column was chosen for the analysis and the column temperature was set at 160°C. Biphenyl was chosen as the internal standard and used the ratio of 1:1 (irradiation product : biphenyl). The retention time for biphenyl was 14.8 minutes and for irradiation product was 6.5 minutes. The response factor was found to be 0.264.

A solution was prepared by dissolving 0.57 g (0.0035 mole) of 1-(3-pyridyl)-2-nitropropene in 400 ml. of 95% undenatured ethanol. The mixture was degassed for one-half hour and then irradiated for two hours with continuous nitrogen flush. After the irradiation, 0.539 g (0.0035 mole) of biphenyl was added into the mixture, and the solution was concentrated under reduced pressure to a total volume of 15 ml. A 2 μl sample of this concentrated solution was injected into the 10% FFAP column of the gas
chromatograph and the relative value of irradiation product to biphenyl was found to be 0.244. Since it was not a well resolved peak, the yield of 1-(3-pyridyl)-1,2-propanedione-1-oxime was estimated to be between 92% and 97%.

(B) Irradiation of 1-(3-pyridyl)-2-nitropropene containing a ten-fold excess of hydrochloric acid and measurement of photochemical rearrangement products

A 10% FFAP column was chosen for the analysis and the column temperature was set at 160°C. The biphenyl was chosen as the internal standard and used in the ratio of 1:1 (irradiation product : biphenyl). The retention time for biphenyl was 14.8 minutes and for irradiation product was 6.5 minutes. The response factor was found to be 0.264.

A solution was prepared by dissolving 0.57 g (0.0035 mole) of 1-(3-pyridyl)-2-nitropropene and 2 g of HCl (37.4%) in 400 ml. of 95% undenatured ethanol. The mixture was degassed for one-half hour and then irradiated for 2 hours with continuous nitrogen flush. After the irradiation 0.539 g (0.0035 mole) of biphenyl was added into the mixture, and the solvent was concentrated under reduced pressure to a total volume of 2 ml. A 2 µl sample of this concentrated solution was injected into the 10% FFAP column of the gas chromatography and the relative value was obtained to be 0.247. Since it was not a well resolved peak, the yield was estimated to be between 93% and 97%.
CHAPTER IV

RESULTS

The method of Robertson\textsuperscript{23} was used to prepare 1-(9-anthryl)-2-nitropropene and the method of Burgen, Stein, Clements\textsuperscript{24} was used to prepare the 1-(3-pyridyl)-2-nitropropene. The structure of these compounds along with their melting points are outlined in Table II. The 1-(3-pyridyl)-2-nitropropene was found to be a severe skin irritant and caused severe dermatosis. We also attempted to synthesize the 1-(2-pyridyl)-2-nitropropene and 1-(4-pyridyl)-2-nitropropene, but the condensation products were very difficult to dehydrate.

Irradiation of 1-(3-pyridyl)-2-nitropropene gave 1-(3-pyridyl)-1,2-propanedione-1-oxime in better than 90\% yield as measured by gas chromatography.

Irradiation of 1-(9-anthryl)-2-nitropropene gave only cis-trans isomerization. Column chromatography of the reaction mixture after two hours irradiation gave 70\% recovery of products consisting of 57\% of the starting isomer (\textit{cis}) and 43\% of the photo-isomer (\textit{trans}). The structure and melting points of the photoproducts are outlined in Table III.

The method of Rosie and Grob\textsuperscript{22} was used to determine the yields of irradiation products from 1-(3-pyridyl)-2-nitropropene. Retention times, G.C. column and column temperature for related compounds are indicated in Table IV. Since the cis-trans isomers of 1-(9-anthryl)-2-nitropropene have the same retention time, the yield could not be determined by using gas chromatography. Column chromatography gave 57\%
of the starting isomer and 43% of the photo-isomer.

The kinetic study was carried out by dissolving 0.0035 mole of 1-(3-pyridyl)-2-nitropropene, with or without added hydrochloric acid, and dissolving 0.0002 mole of 1-(9-anthryl)-2-nitropropene in 400 ml. of 95% unadenatured ethanol. Each solution was irradiated for two hours with nitrogen flush and samples were withdrawn during certain time intervals. The solution was diluted to suitable concentration and was scanned in the u.v./visible spectrum from 400 nm to 200 nm or 650 nm to 300 nm. The kinetic data for these compounds are given in Tables VI through XI. The first order plot of \(-\log(\text{Absorbance})\) vs Time is shown in Figures VIII through XII. The specific rate and half-life are given in Table XII.
### TABLE II
**α, β-UNSATURATED NITRO COMPOUNDS**

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>STRUCTURE</th>
<th>M.P. (°C)</th>
<th>M.P. (°C) (REPORTED)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(9-anthryl)-2-nitropropene</td>
<td><img src="image1" alt="Structure" /></td>
<td>145-146</td>
<td>—</td>
</tr>
<tr>
<td>1-(3-pyridyl)-2-nitropropene</td>
<td><img src="image2" alt="Structure" /></td>
<td>67-68</td>
<td>67.5-68</td>
</tr>
</tbody>
</table>

### TABLE III
**PHOTOPRODUCTS OF IRRADIATION OF α, β-UNSATURATED NITRO COMPOUNDS**

<table>
<thead>
<tr>
<th>MOLECULE</th>
<th>STRUCTURE</th>
<th>M.P. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(9-anthryl)-2-nitropropene</td>
<td><img src="image3" alt="Structure" /></td>
<td>99-101</td>
</tr>
<tr>
<td>1-(3-pyridyl)-1,2-propanedione-1-oxime</td>
<td><img src="image4" alt="Structure" /></td>
<td>210-211</td>
</tr>
</tbody>
</table>
### TABLE IV

G.C. RETENTION TIMES FOR DIFFERENT COMPOUNDS

<table>
<thead>
<tr>
<th>COMPOUNDS</th>
<th>G.C. COLUMN</th>
<th>COLUMN TEMPERATURE (°C)</th>
<th>RETENTION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(9-anthryl)-2-nitropropene</td>
<td>3% Se-30</td>
<td>210</td>
<td>8</td>
</tr>
<tr>
<td>1-(3-pyridyl)-1,2-propanedione-1-oxime</td>
<td>10% FFAP</td>
<td>160</td>
<td>6.5</td>
</tr>
<tr>
<td>biphenyl</td>
<td>10% FFAP</td>
<td>160</td>
<td>14.8</td>
</tr>
</tbody>
</table>

### TABLE V

YIELD OF OXIME OBTAINED BY GAS CHROMATOGRAPHY

<table>
<thead>
<tr>
<th>COMPOUNDS</th>
<th>MOIAR RATIO</th>
<th>RESPONSE FACTOR</th>
<th>% YIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IRRADIATION PRODUCT</td>
<td>INTERNAL STANDARD*</td>
<td></td>
</tr>
<tr>
<td>1-(3-pyridyl)-1,2-propanedione-1-oxime (isolated)</td>
<td>1 : 1</td>
<td>0.2645</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1736**</td>
<td></td>
</tr>
<tr>
<td>1-(3-pyridyl)-1,2-propanedione-1-oxime (irradiation product)</td>
<td>1 : 1</td>
<td>0.2441</td>
<td>92%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1689**</td>
<td>97%</td>
</tr>
<tr>
<td>1-(3-pyridyl)-1,2-propanedione-1-oxime + 10-fold excess of HCl</td>
<td>1 : 1</td>
<td>0.2472</td>
<td>93%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1685**</td>
<td>97%</td>
</tr>
</tbody>
</table>

* Internal standard......biphenyl
** Corrected with base line
**TABLE VI**

U.V./VISIBLE SPECTRAL DATA FOR 1-(9-ANTHRYL)-2-NITROPROPENE FOR T=0 TO T=120 MIN. IRRADIATION TIME.

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>ABSORPTION BAND (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>386, 366, 349, 252</td>
</tr>
<tr>
<td>5</td>
<td>385, 365, 348, 255</td>
</tr>
<tr>
<td>30</td>
<td>383, 363, 346, 255</td>
</tr>
<tr>
<td>60</td>
<td>382, 362, 345, 255</td>
</tr>
<tr>
<td>90</td>
<td>382, 362, 345, 255</td>
</tr>
<tr>
<td>120</td>
<td>382, 362, 345, 256</td>
</tr>
</tbody>
</table>
### TABLE VII

U.V./VISIBLE SPECTRAL DATA FOR 1-(3-PYRIDYL)-2-NITROPROPENE FROM T=0 TO T=120 MINUTES IRRADIATION TIME.

$\lambda_{\text{max}}=292\text{ nm}$

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>*ABSORBANCE OF NO$_2$</th>
<th>-LOG(ABSORBANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.930</td>
<td>0.0315</td>
</tr>
<tr>
<td>5</td>
<td>0.763</td>
<td>0.1180</td>
</tr>
<tr>
<td>10</td>
<td>0.629</td>
<td>0.2013</td>
</tr>
<tr>
<td>15</td>
<td>0.557</td>
<td>0.2541</td>
</tr>
<tr>
<td>30</td>
<td>0.460</td>
<td>0.3372</td>
</tr>
<tr>
<td>80</td>
<td>0.179</td>
<td>0.7471</td>
</tr>
<tr>
<td>110</td>
<td>0.108</td>
<td>0.9666</td>
</tr>
</tbody>
</table>

*ABSORBANCE-absorbance obtained-absorbance of base line
TABLE VIII
U.V./VISIBLE SPECTRAL DATA FOR 1-(3-PYRIDYL)-2-NITROPROPENE PLUS AN EQUAL MOIAR AMOUNT OF HYDROCHLORIC ACID FROM T=0 TO T=120 MINUTES IRRADIATION TIME.

\( \lambda_{\text{max}} = 292 \text{ nm} \)

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th><strong>ABSORBANCE OF NO\textsubscript{2}</strong></th>
<th>-(\log(\text{ABSORBANCE}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.944</td>
<td>0.0250</td>
</tr>
<tr>
<td>5</td>
<td>0.764</td>
<td>0.1169</td>
</tr>
<tr>
<td>10</td>
<td>0.567</td>
<td>0.2449</td>
</tr>
<tr>
<td>15</td>
<td>0.461</td>
<td>0.3363</td>
</tr>
<tr>
<td>30</td>
<td>0.374</td>
<td>0.4271</td>
</tr>
<tr>
<td>60</td>
<td>0.246</td>
<td>0.6038</td>
</tr>
<tr>
<td>100</td>
<td>0.134</td>
<td>0.4271</td>
</tr>
<tr>
<td>120</td>
<td>0.119</td>
<td>0.6038</td>
</tr>
</tbody>
</table>

* ABSORBANCE = absorbance obtained - absorbance of base line
TABLE IX
U.V./VISIBLE SPECTRAL DATA FOR 1-(3-PYRIDYL)-2-NITROPROPENE PLUS A FIVE-FOLD EXCESS OF HYDROCHLORIC ACID FROM T=0 TO T=120 MINUTES IRRADIATION TIME.

\( \lambda_{\text{max}}=292 \text{ nm} \)

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>*ABSORBANCE OF NO₂</th>
<th>-LOG(ABSORBANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.891</td>
<td>0.0501</td>
</tr>
<tr>
<td>5</td>
<td>0.876</td>
<td>0.0575</td>
</tr>
<tr>
<td>10</td>
<td>0.868</td>
<td>0.0615</td>
</tr>
<tr>
<td>15</td>
<td>0.821</td>
<td>0.0857</td>
</tr>
<tr>
<td>30</td>
<td>0.735</td>
<td>0.1337</td>
</tr>
<tr>
<td>60</td>
<td>0.592</td>
<td>0.2277</td>
</tr>
<tr>
<td>120</td>
<td>0.326</td>
<td>0.4868</td>
</tr>
</tbody>
</table>

*ABSORBANCE = absorbance obtained - absorbance of base line
TABLE X

U.V./VISIBLE SPECTRAL DATA FOR 1-(3-PYRIDYL)-2-NITROPROPENE PLUS A TEN-FOLD EXCESS OF HYDROCHLORIC ACID FROM T=0 TO T=120 MINUTES IRRADIATION TIME.

$\lambda_{\text{max}} = 292$ nm

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>*ABSORBANCE OF NO$_2$</th>
<th>-LOG(ABSORBANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.915</td>
<td>0.0386</td>
</tr>
<tr>
<td>5</td>
<td>0.914</td>
<td>0.0391</td>
</tr>
<tr>
<td>10</td>
<td>0.853</td>
<td>0.0641</td>
</tr>
<tr>
<td>15</td>
<td>0.828</td>
<td>0.0820</td>
</tr>
<tr>
<td>30</td>
<td>0.790</td>
<td>0.1024</td>
</tr>
<tr>
<td>60</td>
<td>0.632</td>
<td>0.1993</td>
</tr>
<tr>
<td>90</td>
<td>0.510</td>
<td>0.2922</td>
</tr>
<tr>
<td>120</td>
<td>0.412</td>
<td>0.3815</td>
</tr>
</tbody>
</table>

* ABSORBANCE = absorbance obtained - absorbance of base line
TABLE XI

U.V./VISIBLE SPECTRAL DATA FOR 1-PHENYL-2-NITROPROPENE PLUS A FIVE-FOLD EXCESS OF HYDROCHLORIC ACID FROM T=0 TO T=120 MINUTES IRRADIATION TIME.

\( \lambda_{\text{max}} = 305 \text{ nm} \)

<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
<th>*ABSORBANCE OF NO(_2)</th>
<th>-\log(ABSORBANCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.985</td>
<td>0.0066</td>
</tr>
<tr>
<td>5</td>
<td>0.655</td>
<td>0.1838</td>
</tr>
<tr>
<td>10</td>
<td>0.385</td>
<td>0.4202</td>
</tr>
<tr>
<td>15</td>
<td>0.263</td>
<td>0.5800</td>
</tr>
<tr>
<td>30</td>
<td>0.095</td>
<td>1.0223</td>
</tr>
<tr>
<td>60</td>
<td>0.032</td>
<td>1.4946</td>
</tr>
<tr>
<td>90</td>
<td>0.031</td>
<td>1.5086</td>
</tr>
<tr>
<td>120</td>
<td>0.118</td>
<td>0.9281</td>
</tr>
</tbody>
</table>

*ABSORBANCE=absorbance obtained-absorbance of base line
TABLE XII
SPECIFIC RATE CONSTANT AND HALF-LIFE FOR IRRADIATION PRODUCTS OF UNSATURATED NITRO COMPOUNDS.

<table>
<thead>
<tr>
<th>IRRADIATION PRODUCT</th>
<th>RATE CONSTANT (MIN.(^{-1}))</th>
<th>HALF-LIFE (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-(3-pyridyl)-2-nitropropene</td>
<td>(1.79 \times 10^{-2})</td>
<td>38.6</td>
</tr>
<tr>
<td>1-(3-pyridyl)-2-nitropropene + an equal molar of HCl</td>
<td>(1.37 \times 10^{-2})</td>
<td>50.6</td>
</tr>
<tr>
<td>1-(3-pyridyl)-2-nitropropene + a five-fold excess of HCl</td>
<td>(7.25 \times 10^{-3})</td>
<td>95.5</td>
</tr>
<tr>
<td>1-(3-pyridyl)-2-nitropropene + a ten-fold excess of HCl</td>
<td>(6.93 \times 10^{-3})</td>
<td>100</td>
</tr>
<tr>
<td>1-phenyl-2-nitropropene + a five-fold excess of HCl</td>
<td>(9.12 \times 10^{-2})</td>
<td>7.6</td>
</tr>
<tr>
<td>1-phenyl-2-nitropropene*</td>
<td>(6.58 \times 10^{-2})</td>
<td>10</td>
</tr>
</tbody>
</table>

* Reported by Tang.\(^7\)
FIGURE I

U.V./VISIBILITY SPECTRA OF 1-(9-ANTHRYL)-2-NITROPROPENE (CONC. = 8.32 x 10^{-5} M) IN 95% UNDENATURED ETHANOL UNDER N₂

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
</tr>
</tbody>
</table>
U.V./VISIBLE SPECTRA OF 1-(9-ANTHRYL)-2-NITROPROPENE (CONC. = 6.5 x 10^{-6} M) IN 95% UNDENATURED ETHANOL UNDER N_{2}

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>120</td>
</tr>
</tbody>
</table>
U.V./VISIBLE SPECTRA OF 1-(3-PYRIDYL)-2-NITROPROPENE (CONC.=8.75 x 10^{-5} M) IN 95% UNDENATURED ETHANOL UNDER N₂

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>
U.V./VISIBLE SPECTRA OF 1-(3-PYRIDYL)-2-NITROPROPENE (CONC.=8.75 x 10^{-5} M) CONTAINING AN EQUAL AMOUNT OF HYDROCHLORIC ACID IN 95% UNDENATURED ETHANOL UNDER N_2

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>
U.V./VISIBLE SPECTRA OF 1-(3-PYRIDYL)-2-NITROPROPENE (CONC. = $8.75 \times 10^{-5}$ M) CONTAINING A FIVE-FOLD EXCESS OF HCl IN 95% UNDENATURED ETHANOL UNDER $N_2$

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
</tr>
</tbody>
</table>
U.V./VISIBLE SPECTRA OF 1-(3-PYRIDYL)-2-NITROPROPENE (CONC. = $8.75 \times 10^{-5}$ M) CONTAINING A TEN-FOLD EXCESS OF HCl IN 95% UNDENATURED ETHANOL UNDER N₂

<table>
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<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<tr>
<td>2</td>
<td>30</td>
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<td>3</td>
<td>120</td>
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</tbody>
</table>
FIGURE VII

WAVELENGTH (nm)

U.V./VISIBLE OF 1-PHENYL-2-NITROPROPENE (CONC. = 8.75 x 10⁻⁵ M) CONTAINING A FIVE-FOLD EXCESS OF HCl IN 95% UNDENATURED ETHANOL UNDER N₂

<table>
<thead>
<tr>
<th>NO.</th>
<th>IRRADIATION TIME (MIN.)</th>
</tr>
</thead>
<tbody>
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<td>0</td>
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<tr>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
</tr>
</tbody>
</table>
FIGURE VIII

FIRST ORDER PLOT OF 1-(3-PYRIDYL)-2-NITROPROPENE
FIGURE IX

FIRST ORDER PLOT OF 1-(3-PYRIDYL)-2-NITROPROPENE
CONTAINING AN EQUAL AMOUNT OF HYDROCHLORIC ACID
FIRST ORDER PLOT OF 1-(3-PYRIDYL)-2-NITROPROPENE CONTAINING A FIVE-FOLD EXCESS OF HYDROCHLORIC ACID
FIRST ORDER PLOT OF 1-(3-PYRIDYL)-2-NITROPROPENE
CONTAINING A TEN-FOLD EXCESS OF HYDROCHLORIC ACID
FIRST ORDER PLOT OF 1-PHENYL-2-NITROPROFENE
CONTAINING A FIVE-FOLD EXCESS OF HYDROCHLORIC ACID
CHAPTER V
DISCUSSION

X-ray diffraction studies by Trotter showed the nitro group of 9-nitroanthracence to be twisted out of the plane of the aromatic ring by 85 degrees in the solid state\textsuperscript{11}. The irradiation of 9-nitroanthracence (XXIII) was proposed to undergo nitro-nitrite rearrangement by virtue of the face that the nitro group was forced out of the plane of the aromatic plane by two peri-hydrogens.

The essential factor for the nitro-nitrite rearrangement was believed to be the nitro group twisted out of the aromatic plane for 9-nitroanthracence and out of the ethylene plane for \(\alpha,\beta\)-unsaturated compounds related to \(\beta\)-methyl-\(\beta\)-nitrostyrene.

The irradiation of 1-(2,4,6-trimethylphenyl)-2-nitropropene (LX) and 1-(1-naphthyl)-2-nitropropene (LXI) by Elmore gave only \textit{cis-trans} isomerization with no evidence of nitro-nitrite rearrangement\textsuperscript{10}.
In this study the irradiation of 1-(9-anthryl)-2-nitropropene (LXV) also gave only cis-trans isomerization. The ethylene group lies between two peri-hydrogens which probably forces the ethylene group out of the plane of the aromatic ring. The resonance interaction with the ethylene group would then be very limited or none existent. Therefore, in this non-interacting condition, the photochemistry shows only cis-trans isomerization. This leads one to believe that the ability of the aromatic ring to participate in resonance stabilization is also very important in the nitro-nitrite rearrangement as suggested by Elmore\textsuperscript{10}.

\[
\begin{align*}
\text{(LXV)} & \quad \text{CH}_3 \\
\text{H} & \text{C} &= \text{C} = \text{NO}_2 \\
\text{H} & \text{H} & \text{H}
\end{align*}
\]

\[
\text{(LXVI)} \\
\begin{align*}
\text{H} & \text{C} &= \text{C} = \text{CH}_3 \\
\text{H} & \text{H}
\end{align*}
\]

Pyridine is an analog of benzene in which one of the CH units is replaced by a nitrogen. Various values have been deduced for the empirical resonance energy of pyridine, but it appears to be roughly comparable to benzene\textsuperscript{25}.

In contrast to benzene, m.o. calculations indicate an uneven distribution of electron densities and bond orders. One set of electron densities is shown below\textsuperscript{30}.

\[
\begin{align*}
0.979 & \quad 0.979 \\
1.010 & \quad 1.010 \\
0.951 & \quad 0.951 \\
1.100 & \quad 1.100
\end{align*}
\]
The π-electron densities show that the atoms most affected by the nitrogen atom in the ring are positions 2, 4, and 6.

It would be instructive to compare reactivities of α,β-unsaturated nitro compounds with the ethylene unit attached to the 2, 3 and 4 position of pyridine. Since pyridine is classified as a π-deficient system, one would expect a lower reactivity with the most pronounced effects in the 2 and 4 positions.

Our original plan was to prepare the three compounds described above and study their rate of rearrangement and product distribution. Difficulties encountered in the dehydration of the condensation products of the 2 and 4 isomers coupled with the severe skin irritant properties of these compounds limited our study to the 3-pyridyl isomers.

It was found that 1-(3-pyridyl)-2-nitropropene does indeed undergo the nitro-nitrite rearrangement and at a rate somewhat slower than 1-phenyl-2-nitropropene (1.79 x 10^{-2} compared to 6.58 x 10^{-2}).

The catalytic effect of acid on the photochemistry of unsaturated nitro compounds is well documented. The irradiation of nitrobenzene in isopropyl alcohol has been studied at 366 nm with the quantum yield for the disappearance of nitro group 1.14 x 10^{-2} in degassed solution. The quantum yield studies in 50% isopropyl alcohol-water mixtures containing hydrochloric acid^{28} indicate that protonation in the excited state (triplet) enhances the photochemical disappearance of nitrobenzene. For the irradiation of 1-nitronaphthalene^{29} at 366 nm in 50% isopropyl alcohol-water mixtures no reaction was observed, but solutions containing various concentrations of hydrochloric acid resulted in photoreduction with the formation of 4-chloro-1-naphthylamine. The highest quantum yield
measured was $1.28 \times 10^{-2}$ for 6M HCl with 50% isopropyl alcohol-water. The same result was observed for the irradiation of 4-nitropyridine\textsuperscript{30} ($10^{-2}$ mole) at 273 nm containing 10 ml. HCl in 2-propanol. This gave 4-hydroxyaminopyridine hydrochloride, while in pure 2-propanol there is no detectable reaction. The following scheme is suggested to explain the observed photoreduction of 1-nitronaphthalene (N) in the presence of protons:

\[ N + h\nu \rightarrow N^* \]

\[ N^* \rightarrow N \]

\[ N^* + \text{(CH}_3\text{)}_2\text{CHOH} \rightarrow \text{NH} + \text{CH}_3\text{COH} + H^+ \]

\[ \text{PHOTOPRODUCT} \]

Chow et. al.\textsuperscript{31} reported that irradiation of a methanolic solution of anti-dimer of trans-nitroso-2-piperidinocyclohexane (LXVII) containing hydrochloric acid gave a 65-75% of anti-1-piperidinocyclohexanone oxime (LXVIII). They have suggested the formation of an excited dipolar C-nitroso species which undergoes a facile proton transfer. The facile rearrangement prevented photodisproportionation and dimerization.
Chen\textsuperscript{5} also suggested that water indeed accelerated the photo-
rearrangement of the \( \gamma \)-methyl-\( \gamma \)-nitrostyrene (LXIX) to \( \alpha \)-oximinoketone (LXX) and that probably water is also acting directly upon the excited state of the nitrostyrene.

\[
\begin{align*}
\text{H} & \text{C}=\text{C} \quad \text{NO}_2 \\
\text{H} & \text{C}=\text{C} \quad \text{CH}_3 \\
\text{LXIX} & \\
\text{hv} & \\
\text{H} & \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{NO} & \quad \text{O} \\
\text{hv} & \text{H}_2\text{O} \\
\end{align*}
\]

In contrast to the catalytic effect of added HCl on the photo-
chemistry of unsaturated nitro compounds, it is known that protonation of the nitrogen of the pyridine ring further enhances the \( \pi \)-deficient character of the ring.

The results of added HCl on the reactivity of 1-(3-pyridyl)-2-
nitropropene and 1-phenyl-2-nitropropene are shown in Table XII. It should be noted that addition of a five-fold excess of HCl to 1-phenyl-2-nitropropene prior to irradiation caused the rate of disappearance of the nitro band to increase slightly from \( 6.58 \times 10^{-2} \) to \( 9.12 \times 10^{-2} \). The product distribution appears to be the same in both cases.

A five-fold excess of HCl added to the 1-(3-pyridyl)-2-nitro-
propene system prior to irradiation, however, caused a decrease in
the rate of disappearance of the nitro band from $1.79 \times 10^{-2}$ to $7.25 \times 10^{-3}$. The product distribution appears to be unaltered by the addition of acid. The overall effect can be attributed to the decrease in the availability of $\pi$ electrons to interact with the excited state in the nitro-nitrite rearrangement.
CHAPTER VI
SUMMARY

Steric factors and resonance factors are believed to have a great influence on the nitro-nitrite rearrangement. In our studies of the photochemistry of 1-(9-anthryl)-2-nitropropene we found only cis-trans isomerization. The ethylene group was twisted out of the plane of the aromatic ring by two peri-hydrogens and the resonance stabilization between ethylene group and aromatic ring was hindered. It would appear, therefore, that the nitro-nitrite rearrangement is inhibited.

By adding acid to the 8-methyl-β-nitrostyrene system prior to irradiation, the rate of formation of oximinoketone was found to be 1.3 times the rate for formation of oximinoketone containing no HCl. The acid reported to protonate the excited state of the nitrostyrene and accelerated the rate.

The reverse results were observed for the photochemistry of 1-(3-pyridyl)-2-nitropropene by adding HCl. The rate for formation of oximinoketone in acid is much slower than the rate for formation of oximinoketone without added acid. The acid is believed to protonate the nitrogen atom of the pyridine ring and decrease the resonance stabilization. This would seem to further support the idea that the ability of the aromatic system to interact with the excited state in the nitro-nitrite rearrangement is extremely important.
BIBLIOGRAPHY