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Photochemistry of Heteroaromatic Analogs of β-Methyl-β-Nitrostyrene

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Dale E.

1978
PHOTOCHEMISTRY OF HETEROAROMATIC ANALOGS OF \( \beta \)-METHYL-\( \beta \)-NITROSTYRENE

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
Dale E. Willis
December 1978
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PHOTOCHEMISTRY OF HETERODROMATIC
ANALOGS OF 8-METHYL-8-NITROSTYRENE

Recommended 16 OCT 1978
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2-(2-nitropropenyl)thiophene, 2-(2-nitropropenyl)pyrrole, and 2-(2-nitropropenyl) furan were prepared and irradiated in undenatured 95% ethanol and 2% aqueous acetone. The pyrrole derivative was found to undergo a slow photo-decomposition to tars. The thiophene derivative produced 60% of an \(\alpha\)-oximino ketone and 30% of an oxazine cyclization product when irradiated in ethanol. When irradiated in acetone 47% of the oxime was produced in addition to 7% of the oxazine. The furan derivative produced 12% of an \(\alpha\)-oximino ketone and 51% of an oxazine cyclization product when irradiated in ethanol. When irradiated in acetone 15% of the oxime and 32% of the oxazine were produced. The decrease in yields of the oximes, as compared to the near quantitative yields obtained from the irradiation of \(\beta\)-methyl-\(\beta\)-nitrostyrene, is believed to be due to the lowered resonance energy of these heteroaromatic systems. Kinetic studies showed that more than one mechanism is in operation. Solvent studies showed that acetone plays a definite role in promoting the nitro-nitrite rearrangement.
CHAPTER I
INTRODUCTION

The photorearrangement of 8-methyl-8-nitrostyrene (XLVIII) was first observed in 1964 by Chapman and co-workers. Irradiation of XLVIII in styrene and in tetramethylethylene gave 1-phenyl-1,2-propanedione-1-oxime (XLIX) in 79% yield.

In 1966 Chapman, Cleveland, and Hoganson suggested that the rearrangement to the α-oximino ketone might be photosensitized by acetone. However, in 1965, Saito, Takami, and Matsuura reported that the product distribution from the irradiation of substituted α-nitrostyrenes was independent of the irradiation solvent. The effect of various solvents on the reaction was studied by Chen with the conclusion that acetone is not necessary as a photosensitizer. However, it was noted that the amount of water in the solvent had a large effect on the yield of oxime obtained.

Also, in 1975, Salisbury and co-workers investigated the photorearrangement of E-1-(9-phenanthryl)-2-nitroprop-1-ene (L) to a unique furan derivative (LI). This reaction was found to be sensitized by camphorquinone.

Substituent effects have been investigated by Pinhey and Rizzardo, by Tang, by Matsuura and co-workers, and by Kassaee. It was found that electron withdrawing groups
at the meta- and para-positions inhibit formation of α-oximino ketones and promote cleavage of the styrene. Also observed was the fact that electron donating substituents at the ortho-position promoted the formation of α-oximino ketones. This can be seen through the substitution of a methyl or methoxy group at various positions on the phenyl ring. Kassaee observed first order rate constants of $6.06 \times 10^{-2}$ and $6.89 \times 10^{-2}$ for rearrangement of the ortho-methoxy and ortho-methyl derivatives respectively. $^8$ Tang has recorded rate constants of $7.02 \times 10^{-2}$ and $9.30 \times 10^{-2}$ for rearrangement of the para-methoxy and para-methyl derivatives respectively. $^7$

Elmore has investigated steric effects on the rate of rearrangement and found that a β-alkyl or β-aryl group is a necessary constituent for the nitro-nitrite rearrangement to occur. $^9$ It was also found that, although rate increased significantly on going from a methyl to ethyl group at the β-position, substitution of groups larger than the β-ethyl group had little additional affect on rate. However, Elmore did note a relative rate of 1.68 for the formation of 1-(β-naphthyl)-1,2-propanedione-1-oxime, as compared to the rate of formation of 1-phenyl-1,2-propanedione-1-oxime, which he attributed to the increased aromaticity of the naphthyl group over the phenyl group. He also notes the decreasing tendency toward photorearrangement in the series; 9-nitroanthracene, 2,3-dimethyl-1-nitronaphthalene, and 2,4,6-trimethylnitrobenzene.
The purpose of this study was to investigate the effects of changing the aromaticity of the aryl group of various styrenes and to note the effect on the product distribution and rate of the nitro-nitrite rearrangement. Solvent effects were also briefly studied. Three heteroaromatic derivatives were prepared and irradiated in both 95% ethanol and aqueous acetone. Kinetic data were recorded for the disappearance of the nitro group and the product distribution was analyzed.
Prior to 1964, the photochemistry of alpha,beta-unsaturated nitro compounds received little attention. In 1884, Priebs first observed the photodimerization of beta-nitrostyrene in the solid state. This photodimerization was later reinvestigated by Miller and by Campbell and Ofstead. Irradiation of trans-beta-nitrostyrene (I) was found to produce 1-trans-3-diphenyl-2-cis-4-trans-dinitrocyclobutane (II).

It is of interest to note that attempted photodimerization of trans-beta-nitrostyrene (I) in solution gave only the cis-isomer (III). Cis-trans isomerization of several similar unsaturated nitro compounds has also been reported by Bluhm and Winstein.
In 1959, Parham and co-workers irradiated 2-nitrobenzo-1,4-dithiadiene (IV) in the solid state and obtained the products V and/or VI of undetermined stereochemistry.\textsuperscript{14}

Cridland and Reid have observed dimerization of 4-nitro-1-phenyl-1,3-pentadiene (VII) when irradiated in methanol.\textsuperscript{15} The photodimer (VIII) was reported in 78% yield and is the only reported example of photodimerization of an \( \alpha,\beta \)-unsaturated nitro compound in solution phase.
Photocycloaddition of unsaturated nitro compounds with olefins has also been observed. In 1965, Hoganson irradiated trans-$\beta$-nitrostyrene (I) in the presence of tetramethylethylene (IX). The photoreaction produced 1,1,2,2,-tetramethyl-4-phenyl-3-nitrocyclobutane (X). Hoganson has prepared several other substituted cyclobutanes obtaining yields in excess of 50%. This suggests that the reaction occurs with some facility. It is of interest to note that only the trans-substituted cyclobutanes were isolated.

Winstein and co-workers noted the photochromic behavior of 1-phenyl-2-nitroalkenes. A cyclic intermediate (XII) was proposed to occur on irradiation of the cis-isomer (XI). This would easily explain the inability of Hoganson to isolate any cis-substituted cyclobutanes.

In 1956, Buchi and Ayer reported the irradiation of nitrobenzene (XIII) in the presence of 2-methyl-2-butene
(XIV) and in cyclohexene. The reaction produced a multiplicity of products, chief of which were azobenzene (XVI) and carbonyl products. 1,3,2-dioxazolidine (XV) was proposed as an intermediate.

\[
\text{XIII} + \text{XIV} \xrightarrow{h\nu} \left[ \text{IV} \right] \xrightarrow{} \text{XVI} + \text{carbonyl products} + \text{other products}
\]

Formation of this intermediate has been further investigated by Charlton, Liao, and deMayo with the conclusion that an \(n,\pi^*\) triplet state and a two-step electrophilic process are involved in the reaction.

Ortho-nitrotoluene (XVII) is reported to undergo a photoreaction to form an aci-nitro tautomer (XVIII) by way of intramolecular hydrogen abstraction.

Kitaura and Matsuura irradiated 2,4,6-trimethylnitrobenzene (XIX) in dried benzene and recovered only starting material. However, when irradiated in undried benzene
It was postulated that, due to the increased steric hindrance, the ease of progress of aci-nitro tautomer formation is greatly hindered as compared to o-nitrotoluene (XVII). This increased steric hindrance causes the nitro group to be forced out of the plane of the ring. In the $n,\pi^*$ excited state, the half-filled nonbonding orbital of oxygen is in a good position to overlap with an adjacent orbital of the ring. It is in this manner that an oxaziridine ring (XXI) is formed which collapses to the nitrite ester followed by cleavage and hydrogen abstraction to form the product XX.

\[
\begin{align*}
\text{NO}_2 \quad &\quad \text{OH} \\
\text{XIX} &\quad \xrightarrow{h\nu\ \text{undried benzene}} \quad \text{XX}
\end{align*}
\]
The out-of-plane nitro group is deemed to be very important to reactions involving the nitro-nitrite rearrangement. The irradiation of 2-nitronaphthalene (XXII) in 2-propanol with continuous nitrogen flush produced 2-naphthylhydroxylamine (XXIII). However, when 1-nitronaphthalene was irradiated under similar conditions, no change was noted.

![Chemical structure of XXII and XXIII](image)

A π,π* triplet state has been proposed for both of the above two cases.

In 1966, Chapman and co-workers irradiated 1-nitro-2-methylnaphthalene and 1-nitro-2,3-dimethylnaphthalene (XXIV) and found that the nitro-nitrite rearrangement occurred in both cases.24,25

![Chemical structure of XXIV](image)

Chapman and co-workers further investigated the novel rearrangement by irradiating 9-nitronaphthalene (XXV) in the absence of oxygen. The irradiation produced anthraquinone.
(XXVI), the dimer 10,10'-bianthrone (XXVII), and anthraquinone monoxime (XXVIII).

\[
\begin{align*}
\text{XXV} & \quad \text{hv} \quad \text{XXVII 49\%} \quad \text{XXVII 26\%} \quad \text{XXVI 8\%}
\end{align*}
\]

In the cases of both 1-nitronaphthalene and 9-nitroanthracene, the steric hindrance is such that the nitro group is pushed out of the plane of the ring and thus out of conjugation. It is interesting to note that the two peri-hydrogens of 9-nitroanthracene are able to distort the nitro group to the extent that it is almost perpendicular to the ring system. Trotter found that the nitro group is at an angle of 85\% to the ring system in the solid state.\textsuperscript{26} This orientation easily allows an \(n,\pi^*\) excited state and subsequent nitro-nitrite rearrangement.

In 1968, Szarek and co-workers irradiated the carbohydrate nitro-olefin (XXIX) and found that it undergoes rearrangement to XXX.\textsuperscript{27}
Several heteroaromatic nitro compounds have been irradiated in the past. Reid and Hunt have irradiated 2-nitrofuran (XXXI) in acetone and obtained a 79% yield of the product 3-hydroxyimino-2(3H)-one (XXXII). \(^{28}\)

\[
\begin{align*}
\text{XXXI} &\xrightarrow{h\nu} \text{XXXII} \\
& \quad \text{79%}
\end{align*}
\]

2-nitropyrrrole (XXXIII) was also irradiated in acetone and a 15% yield of 3-hydroxyiminopyrrole-2(3H)-one (XXXIV) obtained. \(^{28}\)

\[
\begin{align*}
\text{XXXIII} &\xrightarrow{h\nu} \text{XXXIV} \\
& \quad \text{15%}
\end{align*}
\]

Chen irradiated 2-nitrothiophene (XXXV) in aqueous methanol and failed to obtain the expected rearrangement product (XXXVI). \(^{4}\)

\[
\begin{align*}
\text{XXXV} &\xrightarrow{h\nu} \text{XXXVI} \\
& \quad \text{0%}
\end{align*}
\]

The resonance energies of the previous three heteroaromatic rings are as follows: \(^{29}\)
<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>RESONANCE ENERGY (Kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiophene</td>
<td>29</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>21</td>
</tr>
<tr>
<td>Furane</td>
<td>16</td>
</tr>
</tbody>
</table>

It would seem that, as the resonance energy of the heteroaromatic ring decreases, the compound behaves more like an α,β-unsaturated nitro compound than an aromatic nitro compound. This is seen in the examination of the irradiation of 2-nitronaphthalene, nitrobenzene, and β-methyl-β-nitrostyrene. 2-nitronaphthalene (XXII) and nitrobenzene form hydroxylamines such as XXIII when irradiated. However, β-methyl-β-nitrostyrene undergoes nitro-nitrite rearrangement to form an oximino ketone. A change in reaction mechanism is apparently initiated when the resonance energy of the ring is not strong enough to resist attack on the ring by the excited oxygen and subsequent loss of resonance stabilization.

In 1967, Kancko and co-workers irradiated 4-nitropyridine-1-oxide (XXXVII) under a nitrogen atmosphere and obtained a near quantitative yield of 4-hydroxymopyridine-1-oxide (XXXVIII). When the same irradiation was performed under oxygen, the nitrate of XXXVII was formed in 60 to 65% yield.
Kancko and co-workers also irradiated 3,5-dimethyl-4-nitropyridine-1-oxide (XXXIX) in the presence of $N_2$ and of $O_2$.\footnote{31} In each case only 3,5-dimethyl-4-hydroxypyridine-1-oxide (XL) was formed.

Hunt, Reid, and Taylor have irradiated several heterocyclic nitroalkenes.\footnote{32} Among these are 2-(2-nitroprop-1-enyl) benzofuran (XLI) and 2-(2-nitroprop-1-enyl) indole (XLII). Both were irradiated in acetone and gave rise to their respective 6-hydroxy-1,2-oxazines, (XLIII) and (XLIV).
They propose that the reactions arise from an intermediate such as XLV.

Much work in the investigation of the photochemistry of $\alpha,\beta$-unsaturated nitro compounds has been done with 6-nitro-cholesteryl acetate (XLVI). Pinhey and Rizzardo irradiated this compound in hexane and in aqueous dioxane in 1965. They observed four products as shown below.
The next year, Chapman and co-workers irradiated XLVI in acetone hoping to observe the effect of a sensitizer on the reaction. Quite a different product distribution was obtained. Chapman attributed the appearance of XLVII to the presence of acetone as a sensitizer.

\[
\text{XLVI} \quad \xrightarrow{hV} \quad \text{XLVII} \quad \quad 52\% \quad \quad 22\% \quad \quad 3\%
\]
One year later, Reid and co-workers published results of the irradiation of XLVI in several solvents. The major product of irradiation of XLVI in ethanol was reported to be 3-oximinocholest-4-en-6-one (XLVII) in 38% yield. On the basis of these findings, Reid stated that acetone is not a necessary sensitizer for the formation of the oxime as previously stated by Chapman. Reid also stated that, although sensitization is not essential, the product distribution is highly solvent dependant.

Chapman and co-workers irradiated 8-methyl-8-nitrostyrene (XLVIII) during the course of their investigations and found it to result in formation of 1-phenyl-1,2-propanedione-1-oxime (XLIX).  

\[
\text{XLVIII} \quad \text{h}_\nu \quad \text{XLIX}
\]

Chen irradiated XLVIII in several solvents and found the yield of the rearrangement product (XLIX) was higher in acetic acid, in ethanol, and in 2-propanol than in acetone. This data was presented in support of the proposed nonessentiality of acetone sensitization. It was also noted that water plays a very important role in the rearrangement. Chen found that nearly quantitative yields of the oxime were obtained when irradiation was carried out in aqueous
acetone, ethanol, or methanol. The yield of XLVII in diethyl ether was increased from 45% to 85.6% by the addition of 1% water to the solvent before irradiation. Kassaee noted that ethanol is a better irradiation solvent than either benzene or cyclohexane.

The mechanism of the nitro-nitrite rearrangement of 8-methyl-8-nitrostyrene, as supported by the evidence for the out-of-plane nitro group, is as follows. An oxygen of the nitro group is excited, followed by bonding of that oxygen to the 8-carbon of the double bond. The oxaziridine ring is then opened to the nitrite ester. This is cleaved to form the ketonic radical shown. Radical recombination and tautomerization then complete the sequence to form the keto-oxime.

![Chemical mechanism diagram]

Chen has noted that an analogy to this reaction occurs in the mass spectrometer in that certain aromatic nitro
compounds show an intense peak at an m/e of M-30 due to loss of NO.$^4$

Thus it seemed that the question of sensitization was closed. In 1975, Crosby and co-workers announced the irradiation of E-1-(9-phenanthryl)-2-nitrop-1-ene (L) in dioxane or sensitized with camphorquinone to give the Z isomer (LI) which produces phenanthrene-9-carboxaldehyde (LII) and a nitro-nitrite rearrangement product (LIII).$^5$

\[
\text{L} \xrightarrow{h\nu} \text{LI} \xrightarrow{\text{NO}_2} \text{LII} + \text{LIII}
\]

Substituent effects on the nitro-nitrite rearrangement have also been studied. Pinhey and Rizzardo irradiated cis-\(\alpha\)-nitrostilbene (LIV) in acetone and obtained in high yield a mixture of siomers of benzilmonooxime (LV).$^6$ Cis-\(\alpha,4\)-dinitrostilbene (LVI) was similarly irradiated and only 30\% of the oxime (LVII) obtained.

\[
\text{LIV} \xrightarrow{h\nu} \text{LV}
\]
In 1974, Tang studied the effect of substitution on the phenyl ring of 8-methyl-8-nitrostyrene. An analogous series of substituted styrenes such as LVIII were irradiated where G equaled H, p-CH₃, p-OCH₃, p-Cl, p-NO₂, or m-NO₂.

The rate of oxime (LIX) formation was in the order: p-CH₃ > p-OCH₃ > H > p-Cl. Rate data for the p-NO₂ and m-NO₂ compounds were ambiguous.

Matsuura also studied substituent effects by placing substituents on the phenyl ring of XLVIII at the para-position. It was found that the yield of oxime decreased as electron withdrawing character increased.

Kassaee substituted the phenyl ring with various functional groups at various positions on the ring and found that electron donating substituents at the ortho-position promote nitro-nitrite rearrangement, whereas electron withdrawing substituents at the meta or para-positions inhibit rearrangement. Mechanistically it is possible for the
An oxygen bond to the $\alpha$-carbon forms an N-oxide ring, as proposed by Pinhey and Rizzardo, followed by breakdown to benzaldehyde and the corresponding acid. An oxygen bond to the $\beta$-carbon forms an oxaziridine ring, as proposed by Chapman, leading to oxime formation. Kassaee postulated that electron withdrawing groups promote an oxygen bond to the $\alpha$-carbon, whereas electron donating groups promote an oxygen bond to the $\beta$-carbon.

Elmore has studied the steric factors affecting the nitro-nitrite rearrangement of $\beta$-methyl-$\beta$-nitrostyrene (XLVIII). Results of this study indicate that a $\beta$-alkyl or $\beta$-aryl group is essential to the nitro-nitrite rearrangement. He also noticed that the rate of oxime formation increased significantly on substitution of an ethyl group for the $\beta$-methyl group in XLVIII but groups larger than ethyl do not significantly affect the rate of reaction. Elmore also noted that ortho substitution on the phenyl ring of XLVIII inhibited the rate of rearrangement. When one $o$-methyl group is present, the rate is reduced but the yield remains constant. When two $o$-methyl groups are present, the reaction
to form the α-oximino ketone is completely halted. This suggests that resonance interaction of the 2-nitropropenyl group with the aromatic ring may play a very important role in the nitro-nitrite rearrangement of β-methyl-β-nitrostyrene derivatives.
CHAPTER III
EXPERIMENTAL

I. Instrumentation

Infrared spectra were recorded on a Perkin Elmer Model 710 infrared spectrophotometer using a thin film between sodium chloride plates if the material was a liquid, or preparing a potassium bromide pellet if the material was a solid. Ultraviolet spectra were recorded on a Cary-14 recording spectrophotometer. Nuclear magnetic resonance spectra were recorded on a Varian A-60A NMR spectrophotometer. Mass spectra were obtained through the courtesy of the University of Kentucky Mass Spectrometry Center. Melting points were obtained through the use of a Fisher-Johns melting point apparatus and were reported as uncorrected. Evaporation of solvents was performed under reduced pressure using a rotary evaporator. Gas chromatography was done on a Varian model 1720 dual column instrument equipped with a Varian Model 20 recorder with a model 224 Disc Integrator.

II. Irradiation Apparatus

Irradiations were performed using a Hanovia-type A-36 550 watt medium pressure mercury arc lamp. The lamp was inserted into the immersion well of a jacketed pyrex tube with a 60/50 standard taper joint to accommodate the pyrex
immersion well. The reaction vessel contained three side arm exits to facilitate the use of a thermometer, gas dispersion tube, and a condenser if needed.

The solution was stirred continuously during irradiations using a magnetic stirring bar and external motor. Solutions were flushed with nitrogen for ½ hour before irradiations were begun. Nitrogen gas was allowed to continue flushing the solutions during irradiations. The temperature of the solution was continuously monitored using a Cole-Farmer model 8390-3 electronic thermometer. The temperature was maintained near 35°C by adjusting the flow rate of water through the cooling jacket of the immersion well.

The kinetic studies were done by removing aliquots at various intervals by means of a syringe and diluting a 1.00 ml. aliquot to 100.0 ml. Ultraviolet spectra were then run from 400 nm to 200 nm following the disappearance of the nitro group.

III. Preparation of α,β- Unsaturated Nitro Derivatives

A. Synthesis of 2-(2-nitropropenyl)thiophene

1) The method of Robertson was used to prepare 2-(2-nitropropenyl)thiophene. 9.2 ml. of thiophene-2-carboxaldehyde (0.10 mol.), 9.9 ml. of n-butylamine (0.10 mol.), and 50 ml. of benzene were placed in a 100 ml. round bottom flask. A modified Dean-Stark moisture trap and condenser were attached. The solution was refluxed until the theoretical amount of water (1.8 ml.) was collected. The benzene
was removed by flash evaporation and the solution was allowed to cool to room temperature. 7.2 ml. of nitroethane (0.10 mol.) and 25 ml. of glacial acetic acid were added to the crude Schiff's base. The mixture was allowed to stand overnight at room temperature with continuous stirring. The reaction mixture was then poured over about 100 gm. of ice and the bright yellow needles were collected. The product was recrystallized twice from ethanol to yield 9.50 gm. (56% of the theoretical yield) of the yellow crystals melting at 68-69.5°C (reported 68.5°C). NMR showed a singlet at 2.6 ppm(3H), a singlet at 8.4 ppm(1H), two doublets at 7.5 ppm(1H) and 7.8 ppm(1H) and a multiplet at 7.3 ppm(1H). Mass spectrometry indicated a molecular weight of 169. Infrared spectrophotometry showed prominent peaks at 1670, 1520, 1420, 1320, 870, and 725 cm⁻¹. The structure of 2-(2-nitropropenyl)thiophene is in agreement with these spectra.

2) The method of Susie and Hass was also used to prepare 2-(2-nitropropenyl)thiophene. 2 gm. of thiophene-2-carboxaldehyde (0.02 mol.), 1.5 ml. of nitroethane (0.02 mol.), and 10 drops of n-butylamine were dissolved in 50 ml. of absolute methanol. The solution was refluxed for 8 hours. The methanol was removed by flash evaporation. Yellow crystals formed on cooling and were isolated. Recrystallization from ethanol gave 2.63 gm. of the product (87% yield) melting at 68-69.5°C.
25

B. *Synthesis of 2-(2-nitropropenyl)pyrrole*

1) The method of Robertson was used to prepare 2-(2-nitropropenyl)pyrrole.\(^{35}\) 19.0 gm. of pyrrole-2-carboxaldehyde (0.20 mol.), 20 ml. of n-butylamine (0.20 mol.), and 100 ml. of benzene were placed in a 100 ml. round bottom flask. A modified Dean-Stark moisture trap and a condenser were attached. The solution was refluxed until the theoretical amount of water (3.6 ml.) was collected. The benzene was removed by flash evaporation and the solution allowed to cool to room temperature. 14.5 ml. of nitroethane (0.20 mol.) and 50 ml. of glacial acetic acid were added to the crude Schiff's base. The mixture was flushed with nitrogen and allowed to stand overnight with continuous stirring. It was found that the slight amount of heat supplied by the stirring motor was necessary for satisfactory results. If the reaction is not stirred overnight, only very small amounts of the product are formed. An alternative to leaving the reaction stirring overnight is to maintain a temperature between 50 and 60°C for 1 hour. After heating, the mixture was poured over about 100 gms. of ice. A very dark brown oil settled to the bottom and was removed. A drop of this oil was added to a drop of water to obtain seed crystals. The main mass of the oil was then purified by recrystallizing several times from ethanol. 8.05 gm. of the yellow needles (26% of the theoretical yield) were obtained by melting from 87-88.5°C. NMR shows a singlet at 2.6 ppm(3H), multiplets at 6.6 ppm(1H), 6.9 ppm(1H), and 7.3 ppm(1H).
There are also singlets at 7.5 ppm(1H) and 8.3 ppm(1H).
Mass spectrometry indicates a molecular weight of 152.
Infrared spectrometry shows major peaks at 3400, 1660, 1490, 1280, 1140, 960, and 740 cm\(^{-1}\). The structure of 2-(2-nitropropenyl)pyrrole is in agreement with these spectra.

2) The method of Susie and Hass was also used in the attempt to prepare 2-(2-nitropropenyl)pyrrole. 37 9.51 gm. of pyrrole-2-carboxaldehyde (0.10 mol.), 7.2 ml. of nitroethane (0.10 mol.), and 0.5 ml. of n-butylamine were dissolved in 100 ml. of benzene. The solution was refluxed for 7 hours. At the end of this time, only a black residue remained. This method was deemed unprofitable due to the thermal instability of 2-(2-nitropropenyl)pyrrole.

3) The method of Gairaud and Lappin was also used in the attempt to prepare 2-(2-nitropropenyl)pyrrole: 38 9.51 gm. of pyrrole-2-carboxaldehyde (0.10 mol.), 7.2 ml. of nitroethane (0.10 mol.), and 5 gm. of ammonium acetate were dissolved in 50 ml. of glacial acetic acid. The mixture was refluxed for 3 hours. During refluxing the evolution of a brown gas was noted. After refluxing, only a black residue remained. This method was also deemed unprofitable due to the thermal instability of 2-(2-nitropropenyl)pyrrole.

C. Synthesis of 2-(2-nitropropenyl)furan

1) The method of Robertson was used to prepare 2-(2-nitropropenyl)furan. 35 16.6 ml. of freshly distilled furfural (0.20 mol.), 19.8 ml. of n-butylamine, and 100 ml. of benzene were placed in a 250 ml. round bottom flask. A
modified Dean-Stark moisture trap and a condenser were attached. The solution was refluxed until the theoretical amount of water (3.6 ml.) was collected. The benzene was removed by flash evaporation and the solution was allowed to cool to room temperature. 14.4 ml. of nitroethane (0.20 mol.) and 50 ml. of glacial acetic acid were added to the crude Schiff's base. The mixture was allowed to stand overnight at room temperature with continuous stirring. The reaction mixture was then poured over about 100 gm. of ice. A dark brown oil settled to the bottom and was collected. A drop of the oil was added to a drop of water and scratched to obtain seed crystals. The mass of the oil was crystallized and purified by several recrystallizations from ethanol to yield 18.6 gm. of the bright yellow platelets (60% of the theoretical yield), melting from 47.5 to 49°C (reported 48-49°C). NMR showed singlets at 2.7 ppm(3H) and 8.0 ppm (1H). Doublets appear at 7.8 ppm(1H) and 6.9 ppm(1H). A multiplet appears at 6.7 ppm(1H). Mass spectrometry indicated a molecular weight of 153. Infrared spectrophotometry showed prominent peaks at 1680, 1530, 1405, 1325, 945, and 780 cm⁻¹. The structure of 2-(2-nitropropenyl)furan is in agreement with these spectra.

2) The method of Susie and Hass was also used in the preparation of 2-(2-nitropropenyl)furan. 9.6 gm. of freshly distilled furfural (0.10 mol.), 7.2 ml. of nitroethane (0.10 mol.), and 0.5 ml. of n-butylamine were dissolved in 100 ml. of benzene and refluxed for 2 hours. On cooling, the solution was poured into about 100 gm. of ice. Yellow
crystals formed immediately and were isolated. The product was purified by recrystallization from ethanol to yield 10.4 gm. of yellow plates (68% of the theoretical yield).

IV. The Photochemistry of the Styrene Analogs

A. The Photochemistry of 2-(2-nitropropenyl)thiophene

1.00 gm. of 2-(2-nitropropenyl)thiophene was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 2 hours with continuous nitrogen flush. The temperature of the solution was kept near 35°C by varying the water flow in the immersion well. After irradiation, the solvent was flashed off under reduced pressure. A yellow oil was collected and eluted through a silica gel column with chloroform. Two crystalline substances were isolated. 0.20 gm. of a yellow crystalline solid was obtained by melting from 41-43°C. NMR indicated that this was a mixture of two closely related substances. Singlets appeared at 2.3, 2.5, 7.6, and 8.4 ppm. Doublets appeared at 7.5 and 7.8 ppm. A multiplet appeared at 7.2 ppm. Thin layer, column and gas chromatography were unable to separate the substances. Infrared spectroscopy showed prominent peaks at 1670, 1520, 1420, 1320, 870, and 725 cm⁻¹. This is identical to the I.R. spectrum of the starting material. On sitting at room temperature, the melting point of these crystals slowly changed until it reached 67-69°C. At this time, NMR indicated that only one substance was present. This data is indicative of the formation of a mixture of cis-trans isomers of the starting
compound. 0.034 gm. of a white crystalline substance was isolated from column chromatography and was purified by recrystallization from carbon tetrachloride. The melting point of this product was 106-107°C. Infrared showed prominent peaks at 3200, 1720, 1430, 1380, 1310, 1240, 1080, 1010, and 710 cm⁻¹. NMR showed singlets at 2.6 and 9.3 ppm. Multiplets appeared at 7.3, 7.7, and 8.3 ppm. The structure of 1-thienyl-1,2-propanedione-1-oxime is consistent with these data.

B. The Photochemistry of 2-(2-nitropropenyl)pyrrole

1) In ethanol:

1.00 gm. of 2-(2-nitropropenyl)pyrrole was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 2.5 hours with continuous nitrogen flush. The temperature of the solution was kept near 35°C by varying the water flow in the immersion well. After irradiation, the solvent was flashed off under reduced pressure. Only a black residue remained. Thin layer chromatography showed at least 10 compounds to be present, all in very small amounts, with decomposition to tars having been the major reaction.

2) In acetone:

1.00 gm. of 2-(2-nitropropenyl)pyrrole was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 2.5 hours with continuous nitrogen flush. The temperature of the solution was kept near 35°C by varying the water flow.
in the immersion well. After irradiation, the solvent was flashed off under reduced pressure. A very dark oil was obtained. Thin layer chromatography showed this to consist of several products present in very low concentration, a great amount of tars from decomposition, and a small amount of starting material. The identity of the starting material was confirmed by I.R. and by mixed spotting with the authentic compound.

C. The Photochemistry of 2-(2-nitropropenyl)furan

1.00 gm. of 2-(2-nitropropenyl)furan was dissolved in 450 ml. of un-denatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 1 hour with continuous nitrogen flush. The temperature of the solution was kept near 35°C by varying the water flow in the immersion well. After irradiation, the solvent was flashed off under reduced pressure. A yellow oil was isolated. By adding small amounts of water and chloroform, it was found that three major compounds could be separated. The chloroform fraction was purified by preparative thin layer chromatography. One large bright yellow band and three minor bands were isolated. One of the minor bands was confirmed by thin layer chromatography and infrared spectroscopy of the authentic compound to be furoic acid. An I.R. was taken of the yellow band and displayed prominent peaks at 3200, 1680, 1530, 1400, 1320, 940, and 770 cm\(^{-1}\). This is identical to the I.R. of the starting compound. NMR showed that two closely related substances
were present. Singlets appeared at 2.4, 2.6, and 8.0 ppm.
Doublets appeared at 7.0, 7.7, and 7.8 ppm. A multiplet
appeared at 6.7 ppm. On sitting at room temperature for
several days, the melting point slowly rose and sharpened
until coming to rest at 47-49°C. These data indicate for-
mation of a mixture of cis-trans isomers of the starting
compound.

Preparative thin layer chromatography of the chloro-
form layer also separated a pale yellow oil of low mobility
on the silica gel plate. Infrared spectroscopy of the oil
showed prominent peaks at 3350, 3050, 1730, 1640, 1500,
1380, 1170, 1030, and 760 cm⁻¹. An adequate NMR spectrum
was difficult to obtain due to the small sample size, however,
peaks appeared at 2.5, 7.4, and 7.8 ppm. This established
the aromaticity of the compound. The structure of 1-furyl-
1,2-propanedione-1-oxime is consistent with these data.

The water fraction was flash evaporated to leave a light
yellow oil. Acetone was added to the oil and precipitation
of pale yellow crystals resulted. It was found that this
product decomposed at 120°C. Infrared spectroscopy showed
major peaks at 3350, 2800, 1640, 1400, 1250, 1300, 1260, 970,
890, 810, and 750 cm⁻¹. NMR showed a singlet at 2.2 ppm.
Multiplets appeared at 4.9, 5.9, and 6.8 ppm. The structure
of furo[b-5,6]-6-hydroxy-2,4-dienyl-1,2-oxazine is in agree-
ment with these data. Thin layer chromatography showed that
the water fraction also contained two very minor products
which remain unidentified.
V. Product Distribution analysis

A. Selection of a Method of Analysis

1) Gas chromatography was tried as a method of analysis for all six irradiations performed. Gas chromatography was rejected as the method of choice for several reasons.

   a) At least one major compound, furo[b-5,6]-6-hydroxy-2,4-dienyl-1,2-oxazine, decomposed when heated giving rise to no vapor pressure.

   b) All of the starting compounds were found to be thermally unstable. These compounds are found in isomeric form as products of the photoreactions.

   c) The compounds formed photochemically tailed badly on gas chromatography. Even when the temperature program capability was used, some tailing was noted.

2) Direct isolation and weighing of the compounds formed was considered and rejected for several reasons.

   a) The method is inherently inaccurate when working with small amounts of material. Losses are always realized in manipulation.

   b) Isolation is difficult. Many of the compounds formed are heat and light sensitive. The acidic conditions of column chromatography causes some decomposition of the 6-hydroxy-1,2-oxazines formed.

3) Analysis of nuclear magnetic resonance spectra was chosen as the method to use.

   a) It is a clean method. Very little sample
b) The method is non-destructive to the compounds involved.

c) The methyl protons are easily integrated to give a good indication of yields. NMR integration is generally regarded to be accurate to ± 2%.  

B. Irradiation of 2-(2-nitropropenyl)thiophene

1) In Ethanol:

0.5915 gm. of 2-(2-nitropropenyl)thiophene (0.0035 mol.) was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 2 hours with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a residual brown oil. This was quantitatively taken up in ethanol and diluted to 10.00 ml. A standard solution of 0.5919 gm. of 2-(2-nitropropenyl) thiophene was also prepared by dissolving in ethanol and diluting to 10.00 ml. NMR sample tubes were filled with these solutions and spectra were taken. The standard solution showed a methyl absorption at 2.63 ppm which was integrated to show 115 units of area. The reaction mixture showed a peak at 2.58 ppm, which integrated to 69 units of area, and a peak at 2.23 ppm, which integrated to 35 units of area. These yields, relative to the standard, are 60% and 30% respectively. Minor peaks accounted for another 1 to 2% of the yield.

2) In acetone:
0.5915 gm. of 2-(2-nitropropenyl)thiophene (0.0035 mol.) was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 5 hours with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a residual brown oil. This was quantitatively taken up in ethanol and diluted to 10.00 ml. An NMR tube was filled with this solution and a spectrum taken. The reaction mixture showed a peak at 2.55 ppm, which integrated to 54 units of area, and a peak at 2.23 ppm, which integrated to 8 units of area. These yields, relative to the standard, are 47% and 7% respectively. Minor peaks accounted for another 2 to 3% of the yield.

C. Irradiation of 2-(2-nitropropenyl)pyrrole

1) In Ethanol:

0.5320 gm. of 2-(2-nitropropenyl)pyrrole was dissolved in 450 ml. of undenature 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 5 hours with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a residual black tar. An NMR spectrum of this tar dissolved in ethanol showed a conglomeration of peaks present in small amounts. It was found unfeasable to separate, identify, and measure yields on these products. The major reaction is decomposition.

2) In Acetone:

0.5320 gm. of 2-(2-nitropropenyl)pyrrole was dissolved
in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 5 hours with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a residual black tar. An NMR spectrum of this tar dissolved in ethanol showed a peak due to the starting material surrounded by many other smaller peaks. It was estimated that the starting material was present in about 10% yield. It was found unfeasable to separate, identify, and measure yields on these products. The major reaction is decomposition.

D. Irradiation of 2-(2-nitropropenyl)furan

1) In Ethanol:

0.5355 gm. of 2-(2-nitropropenyl)furan (0.0035 mol.) was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 1 hour with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a yellow oil. This was quantitatively taken up in ethanol and diluted to 10.00 ml. A standard solution of 0.5355 gm. of 2-(2-nitropropenyl)furan was also prepared by dissolving in ethanol and diluting to 10.00 ml. NMR sample tubes were filled with these solutions and spectra were taken. The standard solution showed a methyl absorption at 2.63 ppm which was integrated to 111 units of area. The reaction mixture showed a peak at 2.52 ppm, which integrated to 14 units of area, and a peak at 2.23 ppm, which
integrated to 56 units of area. These yields, relative to the standard, are 12% and 51% respectively. Minor peaks accounted for another 13% of the yield.

2) In Acetone:

0.5355 gm. of 2-(2-nitropropenyl)furan (0.0035 mol.) was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 1 hour with continuous nitrogen flush. The solvent was flash evaporated under reduced pressure after irradiation to leave a yellow oil. This was quantitatively taken up in ethanol and diluted to 10.00 ml. An NMR sample tube was filled with this solution and a spectrum taken. The reaction mixture showed a peak at 2.52 ppm, which integrated to 17 units of area, and a peak at 2.23 ppm, which integrated to 36 units of area. These yields, relative to the standard, are 15% and 32% respectively. Minor peaks accounted for another 13% of the yield.

VI. Kinetic Studies

A. Irradiation of 2-(2-nitropropenyl)thiophene

1) In Ethanol:

0.5915 gm. of 2-(2-nitropropenyl)thiophene (0.0035 mol.) was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 2 hours with continuous nitrogen flush. Samples were taken at 0, 5, 10, 15, 30, 45, 60, 90, and 120 minutes elapsed irradiation time. 100 ml. aliquots were diluted to 1.00 ml. with undenatured 95% ethanol. The
ultraviolet scan of these samples showed the absorption band at 348 nm to be gradually disappearing over the 2 hour time span. A plot of the absorbance versus time was made and is shown in Figure VII.

2) In Acetone:

0.5915 gm. of 2-(2-nitropropenyl)thiophene (0.0035 mol.) was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 4 hours with continuous nitrogen flush. Samples were taken at 0, 5, 10, 15, 30, 60, 120, and 240 minutes elapsed irradiation time. 1.00 ml. aliquots were diluted to 100.0 ml. with undenatured 95% ethanol. The ultraviolet scan of those samples showed the absorption band at 348 nm to be gradually disappearing over the 4 hour time span. A plot of the absorbance versus time was made and is shown in Figure VIII.

B. Irradiation of 2-(2-nitropropenyl)pyrrole

1) In Ethanol:

0.5320 gm. of 2-(2-nitropropenyl)pyrrole (0.0035 mol.) was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 5 hours with continuous nitrogen flush. Samples were taken at 0, 5, 10, 15, 30, 60, 120, 180, 240, and 300 minutes elapsed irradiation time. 1.00 ml. aliquots were diluted to 100.0 ml. with undenatured 95% ethanol. The ultraviolet scan of these samples showed the absorption band at 398 nm to be disappearing quickly for the first 1.5 hours.
and more slowly thereafter. A plot of the absorbance versus time was made and is shown in Figure IX.

2) In Acetone:

0.5320 gm. of 2-(2-nitropropenyl)pyrrole (0.0035 mol.) was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 4 hours with continuous nitrogen flush. Samples were taken at 0, 5, 10, 15, 30, 60, 120, 180, and 240 minutes elapsed irradiation time. 1.00 ml. aliquots were diluted to 100.0 ml. with undenatured 95% ethanol. The ultraviolet scan of these samples showed the absorption band at 398 nm to be gradually disappearing over the entire irradiation time. A plot of the absorbance versus time was made and is shown in Figure X.

C. Irradiation of 2-(2-nitropropenyl)furan

1) In Ethanol:

0.5355 gm. of 2-(2-nitropropenyl)furan (0.0035 mol.) was dissolved in 450 ml. of undenatured 95% ethanol. The solution was flushed with nitrogen for 30 minutes and then irradiated for 1 hour with continuous nitrogen flush. Samples were taken at 0, 5, 11, 15, 30, and 60 minutes elapsed irradiation time. 1.00 ml. aliquots were diluted to 100.0 ml. with undenatured 95% ethanol. The ultraviolet scan of these samples showed the absorption band at 348 nm to be disappearing quickly for the first 20 minutes and more slowly thereafter. A plot of the absorbance versus time was made and is shown in Figure XI.
2) In Acetone:

0.5355 gm. of 2-(2-nitropropenyl)furan (0.0035 mol.) was dissolved in 450 ml. of 2% aqueous acetone. The solution was flushed with nitrogen for 30 minutes and then irradiated for 1 hour with continuous nitrogen flush. Samples were taken at 0, 5, 10, 15, 30, and 60 minutes elapsed irradiation time. 1.00 ml. aliquots were diluted to 100.0 ml. with undenatured 95% ethanol. The ultraviolet scan of these samples showed the absorption band at 348 nm to be disappearing quickly for the first 20 minutes and more slowly thereafter. A plot of the absorbance versus time was made and is shown in Figure XII.
CHAPTER IV
RESULTS

Three heteroaromatic α,β-unsaturated nitro compounds were prepared. The melting points and structures of these compounds, along with the melting points and structures of their photoproducts, are tabulated in Table I. The starting compounds were synthesized by the method of Robertson. The method of Susie and Hass was also used successfully in the preparation of the thiophene and furan derivatives. The methods of Gairaud and Lappin and of Susie and Hass were tried unsuccessfully in the preparation of the pyrrole derivative.

The photoproducts were prepared by ultraviolet irradiation of the appropriate α,β-unsaturated nitro compound using the method of Tang. Oximes and cyclization products were obtained from 2-(2-nitropropenyl)thiophene and 2-(2-nitropropenyl)furan. Melting points are tabulated in Table I. 2-(2-nitropropenyl)pyrrole yielded a mixture of minor products when irradiated in ethanol. When irradiated in acetone the pyrrole derivative yielded a small amount of the starting compound in addition to many minor products.

Mass spectral data on the three heteroaromatic α,β-unsaturated nitro compounds is shown in Table II.
The chemical shifts of the methyl protons of the starting compounds and their photoproducts are shown in Table III.

Yields of irradiation products were obtained through the use of the integration capability of NMR spectroscopy. In each case 0.0035 mols. of an α,β-unsaturated compound was irradiated and prepared for NMR analysis as previously described in the experimental section. Standard solutions were also prepared. The yields of compounds formed have been tabulated in Table IV.

Kinetic data were recorded by irradiating 0.0035 mols. of the appropriate α,β-unsaturated nitro compound in either ethanol or acetone. The reactions were followed by the disappearance of the nitro band in the U.V. spectrum. The compounds were irradiated various lengths of time as dictated by the reaction kinetics. These spectra are shown in Figures V through X. Plots of absorbance versus time were made. These are shown in Figures VII through XII.
### TABLE I

MASS SPECTRAL DATA

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<th>COMPOUND NAME</th>
<th>MOLECULAR WEIGHT</th>
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<td>169</td>
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<td>2-(2-nitropropenyl)pyrrole</td>
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<td>152</td>
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<td>STRUCTURE</td>
<td>M.P. (°C)</td>
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<tr>
<td>-------------------------------------</td>
<td>-----------------------------</td>
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<td>Thiopheno[b-5,6]-6-hydroxy-2,4-dienyl-1,2-oxazine</td>
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TABLE IV

YIELDS OF THE VARIOUS COMPOUNDS PRODUCED

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<th>YIELD IN ACETONE</th>
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<tr>
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<tr>
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<tr>
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<tr>
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<tr>
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<tr>
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</tr>
<tr>
<td>**</td>
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<td>15%</td>
</tr>
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</tr>
<tr>
<td>**</td>
<td>51%</td>
<td>32%</td>
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* These compounds appear in greater yield on standing for a period of time at room temperature.

** These compounds disappear on standing for a period of time at room temperature.
TABLE V

U.V./VISIBLE SPECTRAL DATA FOR 2-(2-NITROPROPENYL) THIOPHENE IRRADIATED IN ETHANOL FROM T=0 TO T=120 MINUTES IRRADIATION TIME
\( \lambda_{\text{max}} = 348 \text{ nm} \)

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<th>TIME (MIN.)</th>
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<td>30</td>
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<td>0.100</td>
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<tr>
<td>120</td>
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* Corrected absorbance (Absorbance at T=x minus Absorbance at T=120).
**TABLE VI**

U.V./VISIBLE SPECTRAL DATA FOR 2-(2-NITROPROPENYL) THIOPHENE IRRADIATED IN ACETONE FROM T=0 TO T=240 MINUTES IRRADIATION TIME

$\lambda$ max = 348 nm

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<td>240</td>
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* Corrected absorbance (Absorbance at T=x minus Absorbance at T=300).
**TABLE VII**

U.V./VISIBLE SPECTRAL DATA FOR 2-(2-NITROPROPENYL) PYRROLE IRRADIATED IN ETHANOL FROM T=0 TO T=5 HOURS IRRADIATION TIME

$\lambda_{\text{max}} = 398\ \text{nm}$

<table>
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<tr>
<th>TIME (HOURS)</th>
<th>A*</th>
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</thead>
<tbody>
<tr>
<td>0</td>
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<tr>
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<td>4</td>
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<tr>
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</tr>
</tbody>
</table>

* Corrected absorbance (Absorbance at $T=x$ minus Extrapolated Absorbance at Completion of Reaction).
TABLE VIII

U.V./VISIBLE SPECTRAL DATA FOR 2-(2-NITROPROPENYL) PYRROLE IRRADIATED IN ACETONE FROM T=0 TO T=5 HOURS IRRADIATION TIME
λ max = 398 nm

<table>
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<th>TIME (HOURS)</th>
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<tr>
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</table>

* Corrected absorbance (Absorbance at T=x minus Absorbance at T=5 hrs.).
<table>
<thead>
<tr>
<th>TIME (MIN.)</th>
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<tr>
<td>120</td>
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</tbody>
</table>

* Corrected absorbance (Absorbance at T=x minus Absorbance at T=60 minutes).
**TABLE X**

U.V./VISIBLE SPECTRAL DATA FOR 2-(2-NITROPROPENYL) FURAN IRRADIATED IN ACETONE FROM T=0 TO T=60 MINUTES IRRADIATION TIME
λ max = 348 nm

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<tr>
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<tr>
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</table>

* Corrected Absorbance (Absorbance at T=x minus Absorbance at T=60 minutes).
Photochemistry of 2-(2-nitropropenyl)thiophene in 95% EtOH

<table>
<thead>
<tr>
<th>No.</th>
<th>Irradiation time, (min.)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>2</td>
<td>30</td>
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<tr>
<td>3</td>
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</table>
Photochemistry of 2-(2-nitropropenyl)thiophene in aqueous acetone

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<tbody>
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</tr>
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<td>4</td>
<td>240</td>
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</table>
Photochemistry of 2-(2-nitropropenyl)pyrrole in 95% EtOH

<table>
<thead>
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</thead>
<tbody>
<tr>
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<td>1</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
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</tbody>
</table>
Photochemistry of 2-(2-nitropropenyl)pyrrole in aqueous acetone

<table>
<thead>
<tr>
<th>No.</th>
<th>Irradiation time, (min.)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0</td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
<td>4</td>
<td>60</td>
</tr>
<tr>
<td>5</td>
<td>120</td>
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</table>
Photochemistry of 2-(2-nitropropenyl)furan in 95% EtOH

<table>
<thead>
<tr>
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<th>Irradiation time, (min.)</th>
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<tbody>
<tr>
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<td>0</td>
</tr>
<tr>
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<tr>
<td>3</td>
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<td>4</td>
<td>60</td>
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</table>
Photochemistry of 2-(2-nitropropenyl)furan in aqueous acetone

<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>15</td>
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<tr>
<td>3</td>
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<tr>
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<td>60</td>
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</table>
Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)thiophene in ethanol.
Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)thiophene in aqueous acetone.
Figure IX

Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)pyrrole in ethanol.
Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)pyrrole in aqueous acetone.
Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)furan in ethanol.
Plot of absorbance versus time for the irradiation of 2-(2-nitropropenyl)furan in aqueous acetone.
CHAPTER V
DISCUSSION

The photochemical rearrangement of α,β-unsaturated nitro compounds was first discovered in 1964 by Chapman and co-workers. A considerable amount of work has been done on the reaction since that time. Solvent effects have been investigated as well as substituent effects and steric factors.

In investigating substituent effects Pinhey and Rizzardo, Tang, Matsuura, and Kassaee noted that electronic factors played a significant role in the reaction. It was found that electron withdrawing groups at the meta- and para-positions inhibit formation of the α-oximino ketones and promote cleavage of the styrene. Also observed was the fact that electron donating substituents at the ortho-position promote formation of the α-oximino ketones.

The purpose of this investigation has been to irradiate a series of α-aryl-α,β-unsaturated nitro compounds of varying aromaticity and to note the rate and extent of nitro-nitrite rearrangement or the absence of such a reaction for these systems. In performing this task, three heteroaromatic compounds analogous to β-methyl-β-nitrostyrene were irradiated in two solvents. These were the thiophene, pyrrole, and
As furan analogs.

Irradiations were performed in both undenatured 95% ethanol and in 2% aqueous acetone. Irradiation of the pyrrole analog in either solvent led to a large variety of minor products in addition to tars from decomposition. The long irradiation times necessary for the disappearance of the nitro band in the U.V./Visible spectrum, in addition to the product analysis mentioned above, led to the conclusion that a slow photodecomposition was the major photoprocess taking place. In the irradiation of 2-(2-nitropropenyl)thiophene and 2-(2-nitropropenyl)furan, two major products were isolated in addition to various unidentified minor products. One major product isolated in each case was the α-oximino ketone arising directly from a nitro-nitrite rearrangement of the appropriate α,β-unsaturated nitro compound. The yields of the α-oximino ketones from irradiation in ethanol and in acetone are summarized in Table IV.

The second major product arises a bit more obscurely. The photoreaction of each of the α,β-unsaturated nitro compounds in the different solvents was followed through the use of U.V./Visible spectroscopy. Due to the absorbance of several chromophores in the same region as that of the oxime function it was deemed advisable to follow the reaction through the disappearance of the nitro band. The irradiation times necessary for abolishment of the nitro band in each case were used for all further irradiations to insure completion of reaction. However, in the cases of both the thio-
phene and the furan analogs, isolation and purification of the reaction products by column chromatography revealed the presence of a mixture of cis- and trans-isomers of the starting material. The identity of these products was confirmed by I.R., NMR, melting points, and thin layer chromatography. The isomers were found to be inseparable by any method applied. It was also found in each case that one of the isomers was thermally unstable and reverted to the other on standing. Observance of these facts was made through NMR data and melting point data. NMR showed two methyl peaks present at 2.63 and 2.35 ppm in approximately 2:1 ratio respectively for irradiation of the thiophene analog in either solvent. Methyl peaks were present at 2.63 and 2.38 ppm in approximately 1.3:1 ratio respectively for irradiation of the furan analog in either solvent. Later, in the investigation, analyses were performed to determine the yields of the various products by integrating the methyl proton peaks in the NMR spectrum. No isomers of the styrene analogs were detected. However, a water soluble cyclization product was found and identified by I.R. and NMR. In the case of irradiation of 2-(2-nitropropenyl)thiophene, the cyclization product was thiopheno[6,5-b]-6-hydroxy-2,4-dienyl-1,2-oxazine (LXI) and was produced in 30% yield from irradiation in ethanol and in 7% yield from irradiation in aqueous acetone. When 2-(2-nitropropenyl)furan was irradiated, the cyclization product was furo[6,5-b]-6-hydroxy-2,4-dienyl-1,2-oxazine (LXII) and was produced in 51% yield in ethanol and in 32% yield in acetone.
It is our belief that the cyclization products are unstable and give rise, on acid catalysis, to the mixture of cis- and trans-isomers of the starting materials. It is conceivable that a proton could attack the oxazine oxygen in furo[b-5,6]-6-hydroxy-2,4-dienyl-1,2-oxazine (LXII) and cleave the ring to form an oximino ketone such as LXIII. A series of equilibria would then reconvert the intermediate to the starting material.

\[ \text{LXII} \quad \xrightarrow{H^+} \quad \text{LXIII} \]
Isomerization to the more thermodynamically stable isomer would account for the observed conversion of a mixture of isomers to only one isomer. It is reasonable to postulate acid catalysis as the cause of reversion since the mixture of isomers was detected only after column chromatography. Silica gel, which is slightly acidic, was used as the stationary phase.

This is basically the same scheme, in reverse, that Hunt, Reid, and Taylor have postulated upon observance of the furan cyclization product. 32,15

They have also observed similar cyclization products (LXIV and LXV) from the irradiation of 2-(2-nitropropenyl)indole and 2-(2-nitropropenyl)benzofuran.
The cause for the formation of these cyclization products seems to be due to the decrease in resonance energy which allows the aromaticity of the heteroaromatic ring to be broken down more easily. This is easily seen for the monocyclic heteroaromatic systems, which have low resonance energies. However, the polycyclic heteroaromatic systems are less easily understood. The indole system, for example, has a resonance energy of 46.5 kcal/mol. 40 It would seem that this system is more aromatic than benzene and should follow the course of nitro-nitrite rearrangement. The ambiguity is removed by referring to spin density calculations of the indole radical anion system made by Grandclaudon and Lablache-Combier. 41 According to their calculations the pyrrole portion of the indole system contains only 24.5% of the spin density. The major portion of the stability attained by the radical anion is due to the benzene ring. The effective resonance energy in the heteroaromatic ring is therefore quite low.

Elmore noted an analogous situation in the irradiation of o-methyl derivatives of 8-methyl-8-nitrostyrene. 9 The rearrangement reaction was slowed when one o-methyl group
was present and stopped when two o-methyl groups were present. Elmore attributed this behavior to the ability of the o-methyl groups to force the propylene group out of the plane of the aromatic ring and thereby destroy any resonance stabilization obtained from the ring.

The production of small amounts of \( \alpha \)-oximino ketone is to be expected. Cridland, Moles, Reid, and Taylor have irradiated 2-nitropent-2-ene and obtained a 4\% yield of the \( \alpha \)-oximino ketone in this completely nonaromatic system. As mentioned previously, \( \alpha \)-oximino ketones were produced by irradiation of heteroaromatic \( \alpha,\beta \)-unsaturated nitro compounds. The high yields of oxime in the thiophene analog and the low yields of oxime in the furan analog are attributed to the difference in resonance energy between the two systems.

The yield ratios of oximes to oxazines were able to shed light on the question of solvent effects. The yield ratio, defined as \((\text{yield of oxime}/\text{yield of oxazine})\), for the thiophene analog irradiated in ethanol was 2.0. The yield ratio for the thiophene analog irradiated in acetone was 6.7. The yield ratios for irradiation of the furan analog were 0.24 in ethanol and 0.47 in acetone. There does seem to be a definite solvent assistance by acetone in the nitro-nitrite rearrangement, however, as stated by Chen, the assistance does not seem to be significant in the irradiation of more highly aromatic compounds.

Kinetic studies were also performed for the irradiations of the heteroaromatic analogs of \( \beta \)-methyl-\( \beta \)-nitrostyrene in
ethanol and in aqueous acetone. This data is presented in Tables V through X and graphically in Figures I through XII. The major fact to be obtained from this portion of the study is that the reactions are following a complex mechanistic pathway. Tang, Kassaee, and Elmore have noted first order kinetics when the nitro-nitrite rearrangement is the predominant reaction, and a competition between mechanisms when steric or electronic factors interfere with the nitro-nitrite rearrangement.

It would seem that the importance of high resonance energy in the nitro-nitrite rearrangement is firmly established. It would be desirable to investigate the role of solvents further by adding various sensitizers to the reaction and observing any affects on yields or kinetics.
CHAPTER VI
SUMMARY

Several reports have been made attesting to the fact that electronic factors seem to have an influence on the nitro-nitrite rearrangement.\textsuperscript{6,7,8,9} These sources agree that factors which tend to increase resonance stabilization of the initially formed excited state promote the nitro-nitrite rearrangement, whereas factors that decrease resonance stabilization tend to promote other pathways. To investigate this more fully, three heteroaromatic analogs of \(\beta\)-methyl-\(\beta\)-nitrostyrene were prepared and irradiated with U.V light in both ethanol and aqueous acetone. These compounds, in order of decreasing aromaticity, were 2-(2-nitropropenyl) thiophene, 2-(2-nitropropenyl)pyrrole, and 2-(2-nitropropenyl) furan.

Irradiation of the pyrrole analog in either solvent led to a slow photodecomposition to tars. Irradiation of the thiophene analog led to a moderate yield of oxime (40-60%) in either solvent and a low yield of an oxazine cyclization product (7-30%). Irradiation of the furan analog led to a low yield of oxime (12-15%) in either solvent and a moderate yield of the oxazine cyclization product (30-50%). Hunt, Reid, and Taylor have also observed similar cyclization products on irradiation of 2-(2-nitropropenyl)indole and 2-(2-
The lowered resonance energy of the analogs, relative to \( \text{2-(2-nitropropenyl)indole and 2-(2-nitropropenyl)benzofuran} \). The lowered resonance energy of the analogs, relative to \( \text{2-methyl-2-nitrostyrene} \), is presumed responsible for both the decreased yields of oximes and the formation of the cyclization products.

Two solvents were used to investigate solvent effects. The yield ratios of oxime to oxazine show that acetone does promote oxime formation. The yield ratios for the irradiation of \( \text{2-(2-nitropropenyl)thiophene} \) in ethanol and aqueous acetone are 2.0 and 6.7 respectively. The yield ratios for the irradiation of \( \text{2-(2-nitropropenyl)furan} \) in ethanol and aqueous acetone are 0.24 and 0.47 respectively.

Kinetic studies performed on these reactions clearly indicate that more than one mechanism is being followed. This is further evidence that the nitro-nitrite rearrangement is greatly disturbed when the resonance interaction of the excited nitro group with the aromatic ring is decreased or destroyed.
BIBLIOGRAPHY


CORRECTION

PRECEDING IMAGE HAS BEEN
REFILMED
TO ASSURE LEGIBILITY OR TO
CORRECT A POSSIBLE ERROR
B12, F4