6-1976

Photochemistry of beta-Methyl-beta-Nitrostyrene and Its Derivatives

Mohammad Z. Kassaee

Follow this and additional works at: http://digitalcommons.wku.edu/theses
Part of the Chemistry Commons

Recommended Citation
http://digitalcommons.wku.edu/theses/1757

This Thesis is brought to you for free and open access by TopSCHOLAR®. It has been accepted for inclusion in Masters Theses & Specialist Projects by an authorized administrator of TopSCHOLAR®. For more information, please contact topscholar@wku.edu.
PHOTOCHEMISTRY OF beta-METHYL-beta-NITROSTYRENE
AND ITS DERIVATIVES

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
Mohamad Z. Kassaee
June 1976
PHOTOCHEMISTRY OF beta-METHYL-beta-NITROSTYRENE

Recommended 3 Feb 1977

John W. Reamer
Director of Thesis

Robert D. Farina

Approved January 2, 1977

Dean of the Graduate College
ACKNOWLEDGMENTS

To the following persons, I wish to express my humble gratitude and appreciation:

Dr. John W. Reasoner for assigning me this project and for his sincere and unselfish assistance, inspiration and guidance throughout the course of my graduate study.

Dr. Earl F. Pearson for his helpful suggestions and critical reading of the manuscript.

Dr. Gordon Wilson, Jr., for providing the necessary facilities to carry out this study.

Mr. Haj Hadi Kassaee (my brother) for his inspiration, encouragement and financial support.

Mrs. Ameneh Mahrou Kassaee, my wife, for forbearance during the research and typing both the first draft and the final manuscript.

Mrs. Judy Campbell for her assistance and for typing the Greek letters of the final manuscript.
TABLE OF CONTENTS

Chapter

I. INTRODUCTION. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 1
II. HISTORICAL. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 3
III. EXPERIMENTAL. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 25

I. Instrumentation
II. Irradiation
III. Vapor Phase Chromatography
IV. The Organic Synthesis of the β-methyl-β-nitrostyrene
V. The Photochemical Synthesis of the Derivatives of 1-((E)-phenyl)-1,2-propanedione-1-oxime
VI. The Photochemistry of the Derivatives of β-methyl-β-nitrostyrene under N₂
VII. The Kinetics Studies of the Derivatives of β-methyl-β-nitrostyrene under N₂

IV. RESULTS . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 43
V. DISCUSSION. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 65
VI. SUMMARY . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 76
BIBLIOGRAPHY. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 78
**LIST OF FIGURES**

<table>
<thead>
<tr>
<th>I.</th>
<th>Photochemistry of o-methyl-β-methyl-β-nitrostyrene.</th>
<th>57</th>
</tr>
</thead>
<tbody>
<tr>
<td>II.</td>
<td>Photochemistry of o-methoxy-β-methyl-β-nitrostyrene.</td>
<td>58</td>
</tr>
<tr>
<td>III.</td>
<td>Photochemistry of m-methoxy-β-methyl-β-nitrostyrene.</td>
<td>59</td>
</tr>
<tr>
<td>IV.</td>
<td>Photochemistry of p-trifluoromethyl-β-methyl-β-nitrostyrene</td>
<td>60</td>
</tr>
<tr>
<td>V.</td>
<td>First order plot for the irradiation of o-methyl-β-methyl-β-nitrostyrene</td>
<td>61</td>
</tr>
<tr>
<td>VI.</td>
<td>First order plot for the irradiation of o-methoxy-β-methyl-β-nitrostyrene</td>
<td>62</td>
</tr>
<tr>
<td>VII.</td>
<td>First order plot for the irradiation of m-methoxy-β-methyl-β-nitrostyrene</td>
<td>63</td>
</tr>
<tr>
<td>VIII.</td>
<td>First order plot for the irradiation of p-trifluoromethyl-β-methyl-β-nitrostyrene</td>
<td>64</td>
</tr>
</tbody>
</table>


**LIST OF TABLES**

I. Synthesis of Substituted β-methyl-β-nitrostyrene using the method of Lappin ... 45

II. Synthesis of Substituted β-methyl-β-nitrostyrene using the method of Robertson ... 46

III. Synthesis of Substituted 1-phenyl-1,2-propanedione-1-oxime ... 47

IV. Retention times for Different Compounds at 175°C and Average Helium Flow Rate of 140 ml/min. when 20% SE-30 Column is used ... 48

V. Response Factor for the Derivatives of β-methyl-β-nitrostyrene ... 49

VI. Response Factor for Substituted 1-phenyl-1,2-propanedione-1-oxime ... 50

VII. Yield of Oximes (VPC analysis) ... 51

VIII. Spectral Data of o-methyl-β-methyl-β-nitrostyrene ... 52

IX. Spectral Data of o-methoxy-β-methyl-β-nitrostyrene ... 53

X. Spectral Data of m-methoxy-β-methyl-β-nitrostyrene ... 54

XI. Spectral Data of p-trifluoromethyl-β-methyl-β-nitrostyrene ... 55

XII. The Specific Rate Constant and Half-life for the Rearrangement of the Derivatives of β-methyl-β-nitrostyrene ... 56
PHOTOCHEMISTRY OF beta-METHYL-beta-NITROSTYRENE AND ITS DERIVATIVES

Mohamad Z. Kassaee June 1976 78 pages

Directed by: John W. Reasoner
Department of Chemistry Western Kentucky University

o-CH₃, o-CH₃O, m-CH₃O and p-CF₃-beta-methyl-beta-nitrostyrene (compounds not previously reported) were synthesized using the method of Lappin¹³ and Robertson.¹⁴ These styrenes were irradiated in the U.V. region. The yield of corresponding oximes varied from 85 to 100% in aqueous ethanol. This variation in yield of the oximes was attributed to the effect of the substituent on the phenyl rings of the corresponding styrenes. Electron donating substituents promoted the nitro-nitrite rearrangement and electron-withdrawing groups inhibited this rearrangement. A mechanism is proposed for this reaction which unifies and includes ideas proposed by Chapman², Pinhey⁵ and Matsushita³.

The effect of solvent on the irradiation was also studied. The results obtained indicated that the solvent employed does have an effect on the photorearrangement of beta-nitrostyrenes.
CHAPTER I

INTRODUCTION

The photochemical rearrangement of \( \beta \)-methyl-\( \beta \)-nitrostyrene was first observed in 1964 by Chapman and co-workers.\(^1\) Irradiation of \( \beta \)-methyl-\( \beta \)-nitrostyrene with a mercury arc lamp in solvents such as styrene and tetramethylethylene gave 1-phenyl-1,2-propanedione-1-oxime as the major product. It was previously reported that the highest yields of the oxime were obtained using acetone as the irradiation solvent.\(^2\)

More recently Matsuura and co-workers reported that the product distribution obtained from the irradiation of substituted \( \beta \)-methyl-\( \beta \)-nitrostyrenes was independent of the irradiation solvent used.\(^3\)

Solvent effects on the photochemical rearrangement of \( \beta \)-methyl-\( \beta \)-nitrostyrene have been investigated by Chen.\(^4\) It was suggested that acetone, even though a widely used irradiation solvent, is not a required sensitizer for the rearrangement of \( \beta \)-methyl-\( \beta \)-nitrostyrene to 1-phenyl-1,2-propanedione-1-oxime. The amount of water present in the irradiation solvent was found to have a large effect on the yield of oxime obtained in the irradiation.

Substituent effects on the rearrangement have been investigated by Pinhey and Rizzardo,\(^5\) by Tang\(^6\) and by Matsuura and
co-workers. All studies seem to indicate that electron-withdrawing groups tend to inhibit the formation of oxime from the corresponding styrene.

The purpose of this study was to investigate the effect of various substituents on the photochemical rearrangement of $\beta$-methyl-$\beta$-nitrostyrene. Four new derivatives of $\beta$-methyl-$\beta$-nitrostyrene were synthesized and irradiated. The yield of oxime obtained is varied between 85 and 100 percent. This variation is attributed to the effect of the substituent on the phenyl ring of the corresponding styrene. The results obtained in this study are compared to those of Matsurra, Tang and those of Pinhey and Rizzardo.
CHAPTER II
HISTORICAL


The condensation of nitroalkanes (II) with aldehydes (I) to give \( \beta \)-nitrostyrenes (III) is presently the most common method for the synthesis of \( \beta \)-nitrostyrenes.

\[
\text{I} + \text{II} \rightarrow \text{III}
\]

Different catalysts have been used to catalyze the above reaction. In 1883 Priebs carried out this reaction for the first time using an acid catalyst, zinc chloride.\(^7\)

In 1899 Thiele used a basic catalyst, alcoholic postassium hydroxide.\(^8\) A mixture of the aromatic aldehyde (I) and nitromethane (II) (where \( R = H \)) in methanol solution reacted at 10-15\(^{\circ}C\) on addition of a concentrated alkali (KOH in methanol or aqueous NaOH). A nitro-alcohol salt was formed. This reaction product was converted to nitrostyrene by addition of its aqueous solution to an excess of 5N HCl.\(^8,9\)

In 1904 Knoevenagel and Walter used alcoholic methylamine in order to catalyze the above reaction.\(^10\) The reaction
required about one week at room temperature to go to completion. In 1924 Rao and co-workers used ammonium acetate in acetic acid in order to catalyze this condensation. In 1949 Emerson made a comparison between various condensing agents but no evaluation of the various methods to ascertain the most generally useful procedure seems to have been made. In 1952 Catherine B. Gairaud and G. R. Lappin made a comparison of different condensing agents for twenty-four compounds. Although in a few cases the yield of nitrostyrene was lower than with methylamine, it was found substantially better when ammonium acetate in glacial acetic acid was used as the catalyst.

In 1969 Dale N. Robertson studied the primary amine catalyst (IV) used by Knoevenagel for the condensation of aromatic aldehyde (I) with phenyl nitromethane (VI). He outlined the reaction (when primary amine catalyst (IV) is used) in three steps as follows:

A.

\[
\begin{align*}
\text{I} & \quad + \quad \text{H}_2\text{NR} & \quad \leftrightarrow & \quad \text{IV} & \quad + \quad \text{H}_2\text{O} \\
\end{align*}
\]

B.

\[
\begin{align*}
\text{V} & \quad + \quad \text{CH}_2\text{NO}_2 & \quad \leftrightarrow & \quad \text{VI} & \quad \text{VI} \\
\end{align*}
\]
Considering the above reaction sequence, Robertson suggested that in order to make a distinct improvement, water formed in the step A of the reaction sequence must be eliminated, and the basic amine (IV) formed in step B must be tied up. This would exclude by-product formation in accordance with step C of the reaction sequence. By-products formed in reaction sequence C (IX, X, XI, and XIII) are said to be the sources of trouble in the purification; Robertson, therefore, suggested a Schiff's base to be made from aromatic aldehyde and the primary amine and then adding phenylnitromethane in excess glacial acetic acid at room temperature.

\[
\text{PhCH}=\text{NR} + \text{Ph-CH}_2\text{NO}_2 \xrightarrow{\text{CH}_3\text{COOH}} \]

Part B: Photochemistry of $\beta$-nitrostyrenes.

Prior to 1964 the photochemistry of nitrocompounds received little attention. In 1884 Priebs observed the photodimerization of $\beta$-nitrostyrene (XIV) in the solid state.15
In 1927 Seyewetz and D. Mounier discovered that certain nitrocompounds, with different colors, turn brown when exposed to sunlight.\textsuperscript{16} In 1933 Vorozhtsov and Gribov studied the effect of ultraviolet light on various $\beta$-nitro-naphthalene sulfonic acids.\textsuperscript{17} The 1,8-isomer (XVI) was found to be the most sensitive to light.

In 1939 Urbanski and co-workers studied the decomposition of nitroglycerine under the influence of ultraviolet light.\textsuperscript{18} In 1957 Miller irradiated trans-$\beta$-nitrostyrene (XIV) in solution and observed its isomerization to cis-$\beta$-nitrostyrene (XVIII).\textsuperscript{19}
In 1964 Chapman and co-workers reported a photorearrangement of \( \alpha,\beta \)-unsaturated olefins to \( \alpha \)-oximinoketones.\(^1\) Irradiation of 9-nitroanthracene (XIX) for two hours with continuous nitrogen flush (to sweep out gaseous products) gave nitrogen (II) oxide, anthraquinone (XX) 48\%, and anthraquinonemonooxime (XXII) 30\%.

\[
\begin{align*}
\text{XIV} & \quad \xrightarrow{hv} \quad \text{XVII} \\
\text{NO}_2 & \quad \text{hv} \\
\text{XX} & \\
\text{XXI} & + \quad \text{XXII} & + \quad \text{NO}
\end{align*}
\]
Irradiation of 8-methyl-8-nitrostyrene (XXIII) in either styrene or tetramethylene gave 1-phenyl-1,2-propanedione-1-oxime (XXIV) in 79% yield.¹

\[
\text{XXIII} \xrightarrow{hv} \text{XXIV}
\]

The photorearrangement of 9-nitroanthracene (XIX) to anthraquinonemonooxime (XXII) and the other products was explained by Chapman in terms of the following mechanistic path.¹

\[
\text{XIX} \xrightarrow{hv} \text{XX} \xrightarrow{hv} \text{XXV} \xrightarrow{hv} \text{XXVI}
\]
Photoisomerization of the nitrocompound (XIX) gives the nitrite ester (XXV) which can decompose thermally or photochemically to the 9-anthroxyl radical (XXVI) and nitrogen (II) oxide. Dimerization of two 9-anthroxyl radicals would give 10-10'-bianthrone (XXI). Addition of nitrogen (II) oxide to (XXVI) would give the nitrosoketone (XXVII). Isomerization of the nitrosoketone would give anthraquinonemonooxime (XXII). Irradiation of (XXII) gives anthraquinone (XX).
In the presence of $O_2$ the nitrosoketone (XXVII) oxidizes to give nitroanthrone (XXVII).

The photoisomerization of $\beta$-methyl-$\beta$-nitrostyrene (XXIII) to the ketoxime (XXIV) mentioned earlier was rationalized by means of a mechanistic sequence analogous to that given for the nitroaromatic compounds. Initial photoisomerization of (XXIII) gives the nitrite (XXIX). Thermal or photochemical cleavage of the nitrite followed by readdition of nitrogen (II) oxide at the $\beta$-carbon would give the nitrosoketone (XXXI) which could isomerize to give the ketoxime (XXIV).
Kan in 1966 suggested the alternate pathway for the rearrangement of 8-methyl-8-nitrostyrene (XXIII) shown below:

In 1966 Chapman and co-workers postulated that the nitro group must be out of the plane of the ring or double bond in order for the rearrangement to occur. This would permit (in the n,π* excited state) the overlap of the half vacant nonbonding orbital with the adjacent π orbital of the ring or the double bond.
This overlap, which is possible only for the out-of-plane nitro group, leads to the formation of an oxaziridine ring (XXXII) which collapses to the nitrite (XXXIII).

Pinhey and Rizzardo in 1965 irradiated 6-nitrocholesteryl acetate (XXXIV) and did not report any oxime products.\textsuperscript{21}
In 1966 Chapman and co-workers irradiated 6-nitrocholesteryl (XXXIV) in acetone.\(^2\) They observed a different product distribution shown below:
The yield of 3-oximinocholest-4-en-6-one (XXXIX) was 22%. Chapman postulated that acetone was a sensitizer for the photochemical nitro-nitrite rearrangement.

One year later in 1967 Reid irradiated 6-nitrocholesterol acetate (XXXIV) in ethanol. He observed the following product distribution:
Reid obtained a 38% yield of 3-oximinocholest-4-en-6-one (XXXIX) when he irradiated 6-nitrocholesteryl acetate (XXXIV) in ethanol. This was compared to a 22% yield of the same oxime (XXXIX) in acetone obtained by Chapman and none obtained by Pinhey and Rizzardo using hexane and aqueous dioxane as irradiation solvent.

In 1974 Chen attempted to determine whether or not acetone acted as a sensitizer in the irradiation of β-methyl-β-nitrostyrene (XXXIII). β-methyl-β-nitrostyrene (XXXIII) was irradiated in several solvents and it was found that the yield of 1-phenyl-1,2-propanedione-1-oxime (XXIV) was higher in solvents such as acetic acid, ethanol and 2-propanol than in acetone. It was concluded that acetone was not a required synthesizer for nitro-nitrite rearrangement.

Chen also irradiated β-methyl-β-nitrostyrene (XXXIII) in different aqueous solvents and obtained higher yields of (XXIV). The yield of the oxime (XXIV) obtained in diethyl ether was increased from 45% to 85.6% by the addition of 1% water to the solvent prior to irradiation. This led to the
conclusion that water played an important role in the rearrangement. The following role for water was proposed:

\[
\begin{align*}
&\text{XXIII} \\
&\begin{array}{c}
\text{hv} \\
\end{array}
\end{align*}
\]

It is known that polar solvents tend to stabilize the \((n, \pi^*)\) excited state.

Chen also studied the effect of \(O_2\) on the formation of 1-phenyl-1,2-propanedione-1-oxime (XXIII) and observed no oxime (XXIV) formation. The following is the product distribution observed:

\[
\begin{align*}
&\text{XXIII} \\
&\begin{array}{c}
\text{hv} \\
\end{array}
\end{align*}
\]
Irradiation of 1-phenyl-1,2-propanedione-1-oxime (XXIV) under O₂ gas in ethanol, gave no reaction. This suggested that reaction with O₂ occurred prior to the oxime formation. The following mechanistic path was proposed for irradiation of 8-methyl-8-nitrostyrene (XXIII) under O₂.

In 1975 Matsuura and co-workers irradiated 8-nitro styrene (XXIII) under O₂. The following pathway was suggested:
In 1973 Pinhey and Rizzardo studied the substituent effect on the photoisomerization of \( \beta \)-nitrostyrenes to \( \alpha \)-oximinoketones. They found that whereas cis-\( \alpha \)-nitrostilbene (XLVIII) was converted in high yield into a mixture of
isomers of benzilmonooxime (XLIX) (in acetone),

\[
\text{XLVI} \xrightarrow{\text{hr}} \text{XLIX}
\]

under similar conditions cis-\(a,4\)-dinitrostilbene (L) gave only 38\% of the \(a\)-isomer of 2-phenyl-2-hydroxyimino-4-nitroacetophenone (XLIX). The product distribution is as follows:

\[
\text{I} \xrightarrow{\text{hr}} \text{III} 38 \% + 
\]

\[
6 \% \quad \text{XII} + 19 \% \quad \text{XI} + 11 \% \quad \text{III}
\]
The following is suggested by Pinhey and Rizzardo to be the mechanism for formation of products other than the oxime (XLIX) in the above reaction.\textsuperscript{5}

\[ \text{XIX} \xrightarrow{\text{hr}} \text{III} \]

\[ \text{O}_2\text{N}\left(\text{O}^\cdot\text{CN}^\cdot\text{O}\right) + \text{(CHO)} \]

\[ \text{IV} \]

Tang developed a new technique for the synthesis of 1-phenyl-1,2-propanedione-1-oxime and its derivatives by irradiation of the corresponding styrenes in 95\% ethanol.\textsuperscript{6} The yields of the corresponding oximes (analyzed on G.C.) were almost quantitative (90-100\%) except 1-(p-nitrophenyl)-1,2-propanedione-1-oxime and 1-(m-nitrophenyl)-1,2-propanedione-
1-oxime. The results of the kinetic study also showed that p-CH₃, p-CH₃O, or p-Cl-β-methyl-β-nitrostyrene have a faster rate of disappearance of the unsaturated nitro group on irradiation than the p-nitro-(or m-nitro)-β-methyl-β-nitrostyrene. The reason for the formation of low yields of 1-(p-nitrophenyl)-1,2-propanedione-1-oxime and 1-(m-nitrophenyl)-1,2-propanedione-1-oxime and the slower rate of disappearance of the unsaturated nitro group of their corresponding styrenes was attributed to competition between aromatic nitro group attached at the para or meta position and unsaturated β-nitro group during the irradiation. It was also suggested that the excited state or intermediate leading to oxime formation might have been electron deficient since electron donating groups did not appear to hinder the rearrangement and promoted oxime formation.⁶

Recently Matsurra and co-workers investigated the photochemical reactions of a series of substituted (E)-β-methyl-β-nitrostyrenes (XXIII) and proposed that the nitro to nitrite rearrangement leading to the formation of corresponding oximes (XXIV), (path a), and the intermolecular cycloaddition leading to the formation of corresponding aldehydes (XLI), (path b), is taking place competitively from different excited states (XXIX and (XIII)).³
In order to gain insight into the multiplicity of the reaction, the quenching effect of piperylene on the formation of the oxime (XXIV) and the aldehyde (XLVII) was examined in the photoreaction of (E)-3-methyl-3-nitrostyrene (XXII). Addition of piperylene inhibited the formation of the aldehydes (XLVII) but had no effect on the formation of the oxime (XXIV) indicating that there were two different excited states involved. It was proposed that the excited state which was responsible for the formation of the aldehydes (XLVII) (path b) was the lowest triplet state, whereas the unquenchable state responsible for the formation of the oxime (XXIV) was either a singlet state or a higher triplet state. It was
found that nitrostyrenes (XXII) having electron withdrawing substituents ($X=\text{NO}_2$ or Cl) tended to promote the formation of the corresponding aldehydes (XLVII) (path b) while inhibiting the formation of the corresponding oximes (XXIV) (path a). It was also reported that there was no solvent dependency on the product ratio aldehyde/oxime (XLVII/XXIV) for the irradiation of nitrostyrenes (XXII).
I. Instrumentation

The purification of the styrenes and oximes was checked by thin layer chromatography using "Baker-Flex" silica gel. Separation of 1-(m-methoxyphenyl)-1,2-propandione-1-oxime from its reaction mixture was done by column chromatography using a silica gel column. Ultraviolet spectra were recorded on a Cary 14 recording spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer model 457 spectrophotometer. Solid samples were run in carbon tetrachloride solutions. Mass spectra were obtained through the courtesy of the University of Kentucky, Lexington, Kentucky. Evaporation of solvents was done under reduced pressure using a rotary evaporator. Melting points are reported uncorrected on a simple oil-bath melting point apparatus. Vapor phase chromatography was carried out on a Varian model 1720 dual column instrument with disc integrator and temperature programming capability.

II. Irradiation

All irradiations were carried out at an approximate concentration of 0.007 moles of the derivative of 8-methyl-8-nitrostyrene per liter of 95% ethanol. A stream of $N_2$ gas
was bubbled through the solution for at least a half-hour prior to the start of the irradiation. A Hanovia type 673A-36 550-watt medium-pressure mercury arc lamp was used for the light source. The lamp and cooling jacket (pyrex) were fitted into a 550 ml capacity reaction vessel (Ace glass no. 6515) through a 60/50 standard taper joint. The reaction vessel was equipped with three side arm exits near the top to accommodate a thermometer, a condenser, and a dispersion tube for the introduction of gases.

The temperature of the solution was followed during irradiation by a Cole-Parmer model 8390-3 electronic thermometer. The flow of water through the cooling jacket was adjusted to keep the temperature of the solution below 40°C during irradiation.

The progress of the reaction was followed by removing aliquots and recording the ultraviolet spectra. The solution for the ultraviolet spectrophotometer was prepared by diluting 1 ml of aliquots to 100 ml in a volumetric flask. The irradiation was stopped when there was no longer a significant change in absorption.

III. Vapor Phase Chromatography

All vapor phase chromatographic analysis made use of a single column. The five foot column contained 20% SE-30 (silicone gum rubber) on chromosorb W (60/50 mesh). Constant instrument settings were: detector temperature, 300°C; filament current, 150 milliamps; injection port temperature, 240°C; and average helium flow rate 143 ml./min. Oven temperature was 175°C. Retention time agreement and peak enhancement
with authentic samples were obtained for all assigned peaks.

Product yields were obtained by the method of Rosie and Grob. The product count from the disc integrator was divided by the relative response value to obtain a true response value. The true value for the product was divided by the count for the internal standard and multiplied by 100 to obtain the mole percent of the product. The relative response value for each product was determined in the following manner. A solution containing an X:1 mole ratio (X=1, 2 and 3) of product and the internal standard was prepared. A sample of the solution was analyzed by vapor phase chromatography and the count for the product and the internal standard were obtained. The relative response value being the ratio of the product count divided by the internal standard count.

A standard method of analysis was used for the reaction mixture following irradiation. An internal standard was added following irradiation for gas chromatographic analysis. The irradiation mixture containing the internal standard was then concentrated under reduced pressure. The residue was dissolved in acetone (unless otherwise specified) and analyzed.

IV. Synthesis of the Derivatives of \( \beta \)-methyl-\( \beta \)-nitrostyrene.

(A) Synthesis of p-methyl-\( \beta \)-methyl-\( \beta \)-nitrostyrene. The p-methyl-\( \beta \)-methyl-\( \beta \)-nitrostyrene was synthesized by the method of Gairaud and Lappin. A sample of 12.015 g. (0.1 mole) of p-tolualdehyde, 7.5 g. (0.1 mole) of nitroethane, and 5 g. of
ammonium acetate were added to 50 ml. of glacial acetic acid in a 250 ml. boiling flask. The solution was refluxed for three hours and then poured into ice-water. The solid product was collected and recrystallized several times from ethanol. The product weighed 8.51 g. (yield 48%) with m.p. 54.5-55.5°C (reported 24 54.5-55°C). The infrared spectrum for this compound proved to be in satisfactory agreement with the authentic compound.

(B) Synthesis of p-methoxy-β-methyl-β-nitrostyrene.

The p-methoxy-β-methyl-β-nitrostyrene was synthesized by the method of Gairaud and Lappin.13 p-Anisaldehyde (13.615 g., 0.1 mole), nitroethane (7.5 g., 0.1 mole) and 5 g. of ammonium acetate were added to 50 ml. of glacial acetic in a 250 ml. boiling flask. The resulting solution was refluxed for three hours and then poured into ice water. When the precipitation of solid appeared to be complete the mixture was chilled and the product was collected. The solid product was recrystallized from ethanol several times to yield light yellow needles, m.p. 45-46°C reported13,24 m.p. 44-45°C. The yield was 8.98 g. (46.5%). The infrared spectrum for this compound proved to be in satisfactory agreement with the authentic compound.

(C) Synthesis of o-methyl-β-methyl-β-nitrostyrene.

(1) Synthesis using the method of Gairaud and Lappin.13 A solution of 0.1 mole each of o-tolualdehyde (12.015 g.), nitroethane (7.5 g.) and 5 g. of ammonium acetate were added to 50 ml. of glacial acetic acid. The solution was refluxed
for eleven hours and then poured into ice water. A dark oil was obtained. The water was removed and the oil dissolved in hot ethanol and treated with norite A. Refrigeration of the filtrate overnight gave a brown precipitate which was separated from the solution. Recrystallization from ethanol was repeated several times, until 0.89 g. of a deep yellow solid product was collected. The yield was 5% and the melting point was 46-47°C.

(2) Synthesis using the method of Robertson.

Step (1) preparation of the Schiff’s base:

A solution of 0.1 mole each of o-tolualdehyde (12.05 g) and n-butylamine (7.314 g) in 50 ml. of benzene in 100 ml. round bottom flask was attached to a water separator (a modified Dean and Stark moisture trap) and refluxed for one hour until 1.8 ml. of water (the theoretical amount of water) was collected. The solvent was then removed by distillation, finally under aspirator pressure. The crude Schiff’s base was used directly in the next step. Step (2): To a solution of 0.1 mole of nitroethane (7.507 g) in 25 ml. of glacial acetic acid the Schiff’s base (prepared in step 1) was added. The homogeneous mixture was allowed to stand at room temperature overnight. A drop of the mixture was added to a little water in a watch glass and scratched with a glass rod until a few seed crystals were obtained. These were added to the ethanol and treated with norite A. After several recrystallizations from ethanol, 6.20 g. of product (yellow platelets)
was collected (yield 35%). The melting point was 46-47°C. The infrared spectrum and mass spectrum for this compound proved to be satisfactory. The mass spectrum of o-methyl-8-methyl-8-nitrostyrene has been obtained courtesy of University of Kentucky.

(D). Synthesis of o-methoxy-8-methyl-8-nitrostyrene.

(1) Synthesis using Gairaud method.\textsuperscript{13}
o-Anisaldehyde (13.615 g, 0.1 mole), nitroethane (7.5 g, 0.1 mole) and 5 g of ammonium acetate were added to 50 ml. of glacial acetic acid in a 250 ml. boiling flask. The resulting solution was refluxed for twelve hours and then poured into ice water. A dark brown oil was obtained. The oil was separated from water and dissolved in hot ethanol and treated with norite A. The filtrate was refrigerated overnight. A light brown precipitate was formed which was recrystallized from ethanol several times. 1.35 g of the product (yellow needles) was collected (7% yield). The melting point was 50.5-51.0°C.

(2) Synthesis using Robertson method.\textsuperscript{14}
In order to make the appropriate Schiff's base, a solution of 0.1 mole of o-Anisaldehyde (13.615 g) and 0.1 mole of n-butylamine (7.314 g) in 50 ml. of benzene in a 100 ml. round bottom flask was attached to a water separator (a modified Dean and Stark moisture trap) and refluxed for one hour until 1.8 ml. of water (the theoretical amount of water) was collected. The solvent was then removed by distillation. This crude Schiff's base was directly added to a solution of 0.1 mole of nitroethane (7.507 g) in 25 ml of glacial acetic
The homogeneous mixture was allowed to stand overnight. The reaction mixture was then poured into ice water. The solid product was dissolved in ethanol, treated with norite A and filtered. Recrystallization from ethanol and acetic acid several times gave the product that appeared as yellow needles which weighted 6.18 g (yield was 32%). The infrared spectrum and mass spectrum for this compound proved to be satisfactory. The melting point was 50.5-51.5°C. The mass spectrum of o-methoxy-β-methyl-β-nitrostyrene was obtained through the courtesy of the University of Kentucky.

E. Synthesis of m-methoxy-β-methyl-β-nitrostyrene.

(1) Synthesis using Gairaud method.  
A sample of 13.615 g (0.1 mole) of m-Anisaldehyde 7.5 g (0.1 mole) of nitroethane, and 5 g of ammonium acetate were added to 50 ml. of glacial acetic acid in a 250 ml. boiling flask. The resulting solution was refluxed for twelve hours and then poured into ice water. A very dark oil was obtained. Treatment with norite A, recrystallization, chilling and prolonging the reflux time did not result in crystallization of the oil product.

(2) Synthesis using Robertson method.  
A solution of 0.1 mole of m-Anisaldehyde (13.615) and 0.1 mole of n-butylamine (7.314 g) in 50 ml. of benzene in a 100 ml. round bottom flask was attached to a moisture separator (a modified Dean and Stark moisture trap) and refluxed for one hour until 1.8 ml. water (the theoretical amount) was collected. The solvent was then removed by distillation.
This crude Schiff's base was directly added to a solution of 0.1 mole of nitroethane (7.507 g) in 25 ml. of glacial acetic acid. The homogeneous mixture was refluxed under $N_2$ gas for three hours and then poured into ice water. The solid product was dissolved into hot ethanol, treated with norite A and then recrystallized from ethanol several times. 4.44 g of the solid product which had the appearance of yellow needles was collected (yield was 23%). The melting point was 46-47°C. The infrared spectrum and mass spectrum proved satisfactory for $m$-methoxy-$\beta$-methyl-$\beta$-nitrostyrene. The mass spectrum of this compound was obtained courtesy of the University of Kentucky.

F. Synthesis of $p$-trifluoromethyl-$\beta$-methyl-$\beta$-nitrostyrene.

The method of Robertson was used.\textsuperscript{14} A solution each of $p$-trifluoromethylbenzaldehyde (5.47 g, 0.0346 ml) and n-butyamine (2.53 g, 0.346 mol) in 18 ml. of benzene in a 50 ml. round bottom flask was attached to a water separator (a modified Dean and Stark moisture trap) and refluxed for one hour until 0.6 ml. of water (the theoretical amount) was collected. The solvent was then removed by distillation. This crude Schiff's base was added to a solution of 0.0346 mole of nitroethane (2.6 g) in 9 ml. of glacial acetic acid. The homogeneous mixture was refluxed under $N_2$ gas for five hours. A drop of the mixture was added to a little cold water and ethanol in a watch glass and scratched with a glass rod until a few seed crystals were obtained. The reaction mixture was then seeded and scratched. Crystals
and a few drops of oil formed from the solution. The crystals were dissolved in hot ethanol and treated with norite A and the filtrate chilled. The solid crystals after several recrystallizations from ethanol weighed 1.52 g (19% yield). The melting point was 40-41°C. The mass spectrum of p-trifluoromethyl-8-methyl-8-nitrostyrene was obtained through courtesy of the University of Kentucky.

V. Synthesis of the Derivatives of 1-(E)-phenyl-1,2-propanedione-1-oxime.

(A) Synthesis of 1-(p-methylphenyl-)-1,2-propanedion-1-oxime.

2 g of p-methyl-8-methyl-8-nitrostyrene was added to 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with N₂ and the irradiation started. The reaction was stopped after three hours. The solvent was removed under reduced pressure. The concentrate was treated with norite A, hot ethanol and recrystallized from ethanol for several times and also recrystallized from a 50:50 solution of ethanol and benzene. Purification was checked by thin layer chromatography. The residue appearance was white shiny needles. It weighed 0.96 g (48% yield). The melting point was 169-170°C (reported 161-162°C). The infrared spectrum for this compound proved to be in satisfactory agreement with the authentic compound.

(B) Synthesis of 1-(p-methoxyphenyl-)-1,2-propanedion-1-oxime.

A solution was prepared by dissolving 2 g of p-methoxy-8-nitrostyrene in 550 ml. of 95% undenatured ethanol. The
solution was degassed for one-half hour with $N_2$ and the irradiation started. The irradiation time was three hours. The solution was concentrated, decolorized, recrystallized from ethanol several times and also recrystallized from a solution of ethanol and benzene (50:50). Purification was checked by thin layer chromatography. The residue appearance was white needles. It weighed 0.945 g (47.25% yield). The observed melting point was 155-156°C (reported 25 152-153°C). The infrared spectrum of this compound proved to be in satisfactory agreement with the authentic compound.

(C) Synthesis of 1-(o-methylphenyl-)-1,2-propanedione-1-oxime.

A solution was prepared by dissolving 2 g of o-methyl-$\beta$-methyl-$\beta$-nitrostyrene in 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with $N_2$ and the irradiation started. The reaction was stopped after three hours and the solvent removed under reduced pressure. The concentrate was decolorized in hot ethanol and recrystallized from a solution of 50:50 benzene and ethanol. After multiple recrystallization from ethanol, the residue appeared to be white platelets which weighed 0.921 g (46.05% yield). Purification was tested by thin layer chromatography. The melting point was observed to be 139-140°C (the infrared spectrum and the mass spectrum of 1-(o-methylphenyl-)-1,2-propanedione-1-oxime proved to be satisfactory. The mass spectrum of this compound was obtained through the courtesy of the University of Kentucky.
(C) Synthesis of 1-(o-methoxyphenyl)-1,2-propanedione-1-oxime.

A solution was prepared by dissolving 2 g of o-methoxy-
β-methyl-β-nitrostyrene in 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with N₂ and the irradiation started. After three hours irradiation, the solution was concentrated under reduced pressure. The concentrate was decolorized, recrystallized from a 50:50 solution of benzene and ethanol and then recrystallized several times from ethanol. Purification was tested by thin layer chromatography. The white residue weighed 0.930 g (46.5% yield). The melting point was 134-135°C. The mass spectrum and infrared spectrum proved to be satisfactory for this compound. The mass spectrum of 1-(o-methoxyphenyl)-1,2-propanedione-1-oxime was obtained courtesy of the University of Kentucky.

(E) Synthesis of 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime.

A solution was prepared by dissolving 2 g of m-methoxy-
β-methyl-β-nitrostyrene in 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with N₂ and the irradiation started. After three hours irradiation, the resulting black solution was concentrated under reduced pressure. The concentrate was dissolved in benzene and purified by silica gel column chromatography (using benzene as the eluent). In addition to the white residue (oxime) several by-products were noted using thin layer chromatography. The white oxime after recrystallization from ethanol weighed 1.23 g (61.5% yield).
The melting point was 115-116°C. The mass spectrum for 1-(m-methoxyphenyl-)-1,2-propanedione-1-oxime was obtained through the courtesy of the University of Kentucky.

(F) Synthesis of 1-(p-trifluoromethylphenyl-)-1,2-propanedione-1-oxime.

One g. of p-trifluoromethyl-β-methyl-β-nitrostyrene was added to 300 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with N₂ and the irradiation carried out for three hours. The reaction mixture was concentrated under reduced pressure and decolorized. The concentrate was chilled in an ice bath and a few pieces of ice put into the solution. This caused the crystallization to start. The white residue was recrystallized from a 50:50 ethanol-benzene solution, then recrystallized from 95% ethanol. 0.39 g of the white product was collected (yield was 39%). The melting point was 189-189.5°C. The purification was checked by thin layer chromatography (the infrared spectrum and the mass spectrum proved to be satisfactory for this compound). The mass spectrum for 1-(p-trifluoromethylphenyl-)-1,2-propanedione-1-oxime was obtained through the courtesy of the University of Kentucky.

VI. The Photochemistry of the Derivatives of β-methyl-β-nitrostyrene under N₂.

(A) Irradiation of o-methyl-β-methyl-β-nitrostyrene.

A solution was prepared by dissolving 0.6202 g of o-methyl-β-methyl-β-nitrostyrene in 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with
N₂ prior to the irradiation under N₂ with a pyrex immersion well. The sample was irradiated for two hours. The color was observed to be changed from a deep yellow to a light brownish yellow. Benzophenone (0.6320 g) was then dissolved in the reaction mixture. The mixture was then concentrated under reduced pressure and analyzed on a 20% SE-30 column at 175°C. The relative value of the photoproduct and benzophenone was 0.5280. A standard solution containing a 1:1 mole ratio of the pure 1-(o-methylphenyl)-1,2-propanedione-1-oxime and benzophenone was prepared for measuring the response factor. This was found to be 0.5328. The product (oxime) was calculated to be present in 99.10% yield. In addition to 1-(o-methylphenyl)-1,2-propanedione and benzophenone (internal standard) two minor peaks were also noted in the chromatogram.

(B) Irradiation of o-methoxy-8-methyl-8-nitrostyrene.

A solution was prepared by dissolving 0.6762 g of o-methoxy-8-methyl-8-nitrostyrene in 550 ml. of 95% undenatured ethanol. A stream of N₂ gas was passed through the solution for one-half hour. The irradiation using a pyrex immersion well was then carried out for two hours under a continuous stream of N₂. A sample of 0.1322 g of biphenyl was added to the reaction mixture as the internal standard. The reaction mixture was concentrated under reduced pressure and the concentrate was analyzed on a 20% SE-30 column at 175°C. The relative value of the photoproduct (oxime) and biphenyl was 3.172. A standard solution containing a 4:1 mole ratio of the pure 1-(o-methoxyphenyl)-1,2-propanedione-1-oxime
and biphenyl was prepared for measuring the relative response factor. This was found to be 3.180. The photochemical product (oxime) was calculated to be present in 99.75% yield. In addition to 1-(o-methoxyphenyl)-1,2-propanedione-1-oxime and biphenyl (the internal standard) two minor peaks were also noted in the chromatogram.

(C) Irradiation of m-methoxy-β-methyl-β-nitrostyrene.

(1) In 95% undenatured ethanol:
A solution was prepared by dissolving 0.6762 g of m-methoxy-β-methyl-β-nitrostyrene in 550 ml. of 95% undenatured ethanol. The solution was degassed for one-half hour with N₂ and the irradiation (using a pyrex immersion well) started under a continuous stream of N₂. A sample of 0.1053 g of benzophenone was added as the internal standard. The reaction mixture was concentrated under reduced pressure and analyzed on a 20% SE-30 column at 175°C. The relative value of the product and benzophenone was 1.8744. A standard solution containing a 6:1 mole ratio of the pure 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime and benzophenone was prepared for measuring the relative response factor. This was found to be 2.1286. The photo-product (oxime) was calculated to be present in 88.06% yield. During the course of the two hours irradiation the solution color changed from a light yellow to a black color. Seven minor peaks were noted in the chromatogram in addition to 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime and benzophenone.
(2) Irradiation of m-methoxy-β-methyl-β-nitrostyrene in Benzene.

The above procedure was followed using benzene in the place of 95% denatured ethanol as the irradiation solvent. The relative value of the photoproduct (oxime) and benzophenone was 1.398. The photoproduct (oxime) was calculated to be present in 65.68% yield. Comparison of minor peaks of the two chromatograms are as follows: At the fourth minute of the chromatogram using benzene as the irradiation solvent a substantial increase in the size of the peak was observed. In addition, there were six peaks between zero and the first minute of the chromatography using benzene compared to only two peaks observed in the same region when ethanol was used as the irradiation solvent. In addition to 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime and benzophenone (internal standard) twelve minor peaks were also noted in the chromatogram using benzene as irradiation solvent. This is compared to the seven minor peaks when ethanol was used as the irradiation solvent.

(D) Irradiation of p-trifluoromethyl-β-methyl-β-nitrostyrene.

A solution was prepared by dissolving 0.1046 g of p-trifluoromethyl-β-methyl-β-nitrostyrene in 350 ml. of 95% ethanol. A stream of N₂ was passed through the solution for one-half hour prior to and during the irradiation. Immediately following the irradiation, a sample of 0.0804 g. of benzophenone was added as the internal standard. The reaction mixture was concentrated under reduced pressure and the
concentrate was analyzed on a 20% SE-30 column at 175°C. The relative value of the photoproduct (oxime) and benzophenone was 0.720. A standard solution containing a 1:1 mole ratio of the pure 1-(p-trifluoromethylphenyl)-1,2-propanedione-1-oxime and benzophenone was prepared for measuring the relative response factor. This was found to be 0.830. The photoproduct (oxime) was calculated to be present in 86.75% yield. In addition to 1-(p-trifluoromethylphenyl)-1,2-propanedione-1-oxime and benzophenone (the internal standard) two minor peaks were also noted in the chromatogram.

VIII. The Kinetics Studies of Photochemistry of the Derivatives of β-methyl-β-nitrostyrene under N₂.

(A) Photochemical rearrangement of o-methyl-β-methyl-β-nitrostyrene.

A solution of 0.0035 mole of o-methyl-β-methyl-β-nitrostyrene was dissolved in 550 ml. of 95% undenatured ethanol. The solution was stirred continuously and a stream of N₂ passed through the solution prior to (at least one-half hour), during the irradiation and after irradiation (for at least one-half hour). The total irradiation time was 120 minutes. The solution for the ultraviolet spectrophotometer was prepared by diluting a 1 ml. aliquot sample (which was withdrawn every five minutes during irradiation) to 100 ml. with 95% undenatured ethanol. Analysis of the reaction mixture by ultraviolet spectroscopy clearly showed the disappearance of the band at 305 nm. This disappearance was very rapid during the first hour of irradiation. The rate constant
(6.89 x 10^{-2} \text{ min}^{-1}) \) of this disappearance was obtained by plotting \( \log A \) vs. time. The half-life was calculated to be 10.1 minutes.

(B) Photochemical Rearrangement of o-methoxy-\( \beta \)-methyl-\( \beta \)-nitrostyrene.

A solution of 0.0035 mole of o-methoxy-\( \beta \)-methyl-\( \beta \)-nitrostyrene was prepared as described previously. The solution was degassed and irradiated for 120 minutes. The ultraviolet spectrum was recorded for each aliquot sample as the reaction progressed. The absorption at 333.75 nm was shown to disappear quickly. The rate constant \((6.06 \times 10^{-2} \text{ min}^{-1})\) was measured by plotting \( \log A \) vs. time. The half-life was calculated to be 11.4 minutes.

(C) Photochemical Rearrangement of m-methoxy-\( \beta \)-methyl-\( \beta \)-nitrostyrene.

A solution of 0.0035 mole of m-methoxy-\( \beta \)-methyl-\( \beta \)-nitrostyrene was prepared by dissolving the sample in 550 ml of 95\% undenatured ethanol. The solution was degassed with \( \text{N}_2 \) for one-half hour and irradiation started. Aliquots were removed during the progress of the irradiation. One ml of the aliquot was diluted \( \sim 100 \) ml with 95\% undenatured ethanol. The ultraviolet spectrum was recorded. The band at 305 nm disappeared quickly. The specific rate constant of disappearance of the unsaturated nitrogroup was \( 15.8 \times 10^{-2} \text{ min}^{-1} \). The half life of this rearrangement was found to be 4.4 minutes. This was obtained by plotting \( \log A \) vs. time.
(D) Photochemical Rearrangement of p-trifluoromethyl-β-methyl-β-nitrostyrene.

A solution of 0.00455 mole of p-trifluoromethyl-β-methyl-β-nitrostyrene was dissolved in 300 ml. of 95% denatured ethanol. The solution was degassed for one-half hour and the irradiation started while the solution was stirred continuously under a stream of \( N_2 \). The total irradiation time was 120 minutes. The solution for the ultraviolet spectrophotometer was prepared by diluting 1 ml. of aliquot sample to 100 ml. with 95% undenatured ethanol. Analysis of the reaction mixture by ultraviolet spectroscopy clearly showed the disappearance of the band at 288.75 nm. The rate constant \( (10.9 \times 10^{-2} \text{min}^{-1}) \) for this disappearance was obtained by plotting \( \log A \) vs. time. The half-life was calculated to be 6.36 minutes.
CHAPTER IV
RESULTS

Two synthetic pathways were used in the preparation of the derivatives of \( \beta \)-methyl-\( \beta \)-nitrostyrene. The compounds \((p\text{-methyl-}, \ p\text{-methoxy-}, \ o\text{-methyl-})\) and \((o\text{-methoxy-})\-methyl-\( \beta \)-nitrostyrene were synthesised using the method of Gairaud and Lappin.\(^1\) The recrystallized yield of these styrenes and their melting points are summarized in table I. The most satisfactory procedure for the synthesis of \( o\text{-methyl, m-methoxy} \) and \( p\text{-trifluoromethyl-} \beta \text{-methyl-} \beta \text{-nitrostyrene (compounds not previously reported) was found to be the method of Robertson.}\(^1\) The recrystallized yield of the various styrenes (using the Robertson method) and their melting points are summarized in table II.

A solution was prepared by dissolving \( 2 \) g of the derivative of \( \beta \)-methyl-\( \beta \)-nitrostyrene in \( 550 \) ml of \( 95\% \) undenatured ethanol. The solution was degassed for one-hour with \( N_2 \) and the irradiation started. The recrystallized yield and the melting point of the resulting oximes are given in table VII.

A standard technique\(^4\) for the irradiation and analysis of the derivatives of \( \beta \)-methyl-\( \beta \)-nitrostyrene was used. The retention time data is given in table IV. Response factors have been determined for the different styrenes and oximes with different internal standards according to the method of
Rosie and Grob. These are given in tables V and VI. The disc integrator data used to calculate yields of the various oximes is summarized in table VII. When benzene was used instead of 95% undenatured ethanol (as the irradiation solvent for m-methoxy-β-methyl-β-nitrostyrene) the yield of 1-(p-methoxyphenyl)-1,2-propanedione-1-oxime decreased from 88.06% to 65.68%.

A solution of 0.0035 mole of each derivative of β-methyl-β-nitrostyrene in 550 ml of 95% undenatured ethanol was irradiated for two hours. The progress of the reaction was followed by recording the ultraviolet spectrum. The kinetic results are shown in figures I to IV pages 52 to 55. The spectral data for the derivatives of β-methyl-β-nitrostyrene are summarized in tables VIII to XI. The specific rate and half-life of rearrangement of the derivatives of β-methyl-β-nitrostyrene are summarized in table XII. The disappearance is initially a first order reaction (figure V to VIII).
TABLE I
SYNTHESIS OF SUBSTITUTED 8-METHYL-8-NITROSTYRENES
USING THE METHOD OF GAIRAUD AND LAPPIN. 13

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield</th>
<th>MP.(°C)</th>
<th>Appearance</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4-CH₃</td>
<td>48%</td>
<td>54.5-55.5</td>
<td>light yellow needles</td>
<td>C₁₀H₁₁NO₂</td>
</tr>
<tr>
<td>II</td>
<td>4-CH₂O</td>
<td>46.5%</td>
<td>95-46</td>
<td>yellow needles</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>III</td>
<td>2-CH₃</td>
<td>5%</td>
<td>46-47</td>
<td>deep yellow</td>
<td>C₁₀H₁₁NO₂</td>
</tr>
<tr>
<td>IV</td>
<td>2-CH₂O</td>
<td>7%</td>
<td>50.5-51.5</td>
<td>deep yellow</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>V</td>
<td>3-CH₂O</td>
<td>—</td>
<td>—</td>
<td>oil</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
</tbody>
</table>
TABLE II
SYNTHESIS OF SUBSTITUTED β-METHYL-β-NITROSTYRENES
USING THE METHOD OF ROBERTSON. 14

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield</th>
<th>MP. (°C)</th>
<th>Appearance</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-CH₃O</td>
<td>32%</td>
<td>50.5-51.5</td>
<td>yellow small needles</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>II</td>
<td>2-CH₃</td>
<td>35%</td>
<td>46-47</td>
<td>light yellow plates</td>
<td>C₁₀H₁₁NO₂</td>
</tr>
<tr>
<td>III</td>
<td>4-CF₃</td>
<td>19%</td>
<td>40-41</td>
<td>deep yellow plates</td>
<td>C₁₀H₈F₃NO₂</td>
</tr>
<tr>
<td>IV</td>
<td>3-CH₃O</td>
<td>23%</td>
<td>46-47</td>
<td>yellow needles</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
</tbody>
</table>
TABLE III
SYNTHESIS OF SUBSTITUTED 1-PHENYL-1,2-PROPANEDIONE-1-OXIME

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Yield</th>
<th>MP.(°C)</th>
<th>Appearance</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>4-CH₃</td>
<td>48%</td>
<td>169-70</td>
<td>white shining needles</td>
<td>C₁₀H₁₁NO₂</td>
</tr>
<tr>
<td>II</td>
<td>4-CH₂O</td>
<td>48%</td>
<td>155-6</td>
<td>white needles</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>III</td>
<td>2-CH₃</td>
<td>45%</td>
<td>139-40</td>
<td>white plates</td>
<td>C₁₀H₁₁NO₂</td>
</tr>
<tr>
<td>IV</td>
<td>2-CH₂O</td>
<td>47%</td>
<td>134-35</td>
<td>white plates</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>V</td>
<td>3-CH₂O</td>
<td>61.5%</td>
<td>115-16</td>
<td>white plates</td>
<td>C₁₀H₁₁NO₃</td>
</tr>
<tr>
<td>VI</td>
<td>4-CF₃</td>
<td>39%</td>
<td>189-89.5</td>
<td>white plates</td>
<td>C₁₀H₈F₃NO₂</td>
</tr>
</tbody>
</table>

*column chromatography also used for purification.*
TABLE IV
Retention times for different compounds at 175°C and average helium flow rate of 140 ml/min. when 20% SE-30 column is used.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Retention time (in minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-methyl-β-methyl-β-nitrostyrene</td>
<td>8.8</td>
</tr>
<tr>
<td>p-methoxy-β-methyl-β-nitrostyrene</td>
<td>17.4</td>
</tr>
<tr>
<td>o-methyl-β-methyl-β-nitrostyrene</td>
<td>6.4</td>
</tr>
<tr>
<td>o-methoxy-β-methyl-β-nitrostyrene</td>
<td>12.8</td>
</tr>
<tr>
<td>m-methoxy-β-methyl-β-nitrostyrene</td>
<td>14.1</td>
</tr>
<tr>
<td>p-trifluoromethyl-β-methyl-β-nitrostyrene</td>
<td>5.0</td>
</tr>
<tr>
<td>1-((p-methylphenyl)-1,2-propanedione-1-oxime</td>
<td>9.8</td>
</tr>
<tr>
<td>1-((p-methoxyphenyl)-1,2-propanedione-1-oxime</td>
<td>18.8</td>
</tr>
<tr>
<td>1-((o-methoxyphenyl)-1,2-propanedione-1-oxime</td>
<td>19.6</td>
</tr>
<tr>
<td>1-((o-methylphenyl)-1,2-propanedione-1-oxime</td>
<td>10.6</td>
</tr>
<tr>
<td>1-((m-methoxyphenyl)-1,2-propanedione-1-oxime</td>
<td>7.8</td>
</tr>
<tr>
<td>1-((p-trifluoromethylphenyl)-1,2-propanedione-1-oxime</td>
<td>16.8</td>
</tr>
<tr>
<td>o-Anisaldehyde</td>
<td>6.8</td>
</tr>
<tr>
<td>m-Anisaldehyde</td>
<td>2.0</td>
</tr>
<tr>
<td>o-tolualdehyde</td>
<td>0.5</td>
</tr>
<tr>
<td>p-trifluoromethylbezaldehyde</td>
<td>1.0</td>
</tr>
<tr>
<td>Biphenyl</td>
<td>1.4</td>
</tr>
<tr>
<td>Benzophenone</td>
<td>4.5</td>
</tr>
<tr>
<td>Fluoren-9-one</td>
<td>11.2</td>
</tr>
<tr>
<td></td>
<td>18.1</td>
</tr>
</tbody>
</table>
TABLE V
RESPONSE FACTOR FOR THE DERIVATIVES OF 8-METHYL-8-NITOSTYRENE

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Internal Standard</th>
<th>moles ratio (pure styrene/ internal standard)</th>
<th>Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-CH₃</td>
<td>Benzophenone</td>
<td>1:1</td>
<td>1.28</td>
</tr>
<tr>
<td>II</td>
<td>2-CH₃O</td>
<td>Biphenyl</td>
<td>2:1</td>
<td>5.08</td>
</tr>
<tr>
<td>III</td>
<td>3-CH₃O</td>
<td>Benzophenone</td>
<td>1:1</td>
<td>0.89</td>
</tr>
<tr>
<td>IV</td>
<td>4-CF₃</td>
<td>Benzophenone</td>
<td>1:1</td>
<td>1.28</td>
</tr>
</tbody>
</table>
TABLE VI
RESPONSE FACTOR FOR SUBSTITUTED
1-PHENYL-1,2-PROPA NEDIONE-1-OXIME

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Internal Standard</th>
<th>moles ratio (pure oxime internal standard)</th>
<th>Response Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-CH₃</td>
<td>Benzophenone</td>
<td>1:1</td>
<td>0.53</td>
</tr>
<tr>
<td>II</td>
<td>2-CH₃₀</td>
<td>Biphenyl</td>
<td>4:1</td>
<td>3.18</td>
</tr>
<tr>
<td>III</td>
<td>3-CH₃₀</td>
<td>Benzophenone</td>
<td>6:1</td>
<td>2.13</td>
</tr>
<tr>
<td>IV</td>
<td>4-CF₃</td>
<td>Benzophenone</td>
<td>1:1</td>
<td>0.83</td>
</tr>
</tbody>
</table>
TABLE VII

YIELD OF OXIMES OBTAINED (VPC ANALYSIS) BY IRRADIATION OF THE CORRESPONDING STYRENES (AND THE DISC INTEGRATION DATA USED)

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>*Disc Integrator Data</th>
<th>Yield of Oxime</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-CH₃</td>
<td>0.523</td>
<td>99.00%</td>
</tr>
<tr>
<td>II</td>
<td>2-CH₂₀</td>
<td>3.17</td>
<td>99.75%</td>
</tr>
<tr>
<td>III</td>
<td>3-CH₂₀</td>
<td>1.874</td>
<td>88.06%</td>
</tr>
<tr>
<td>IV</td>
<td>4-CF₃</td>
<td>0.72</td>
<td>86.75%</td>
</tr>
</tbody>
</table>

* moles ratio = \( \frac{\text{photoproduct oxime}}{\text{internal standard}} \).
### TABLE VIII

SPECTRAL DATA OF O-METHYL-β-METHYL-β-NITROSTYRENE
AFTER TWO HOURS IRRADIATION

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorption</th>
<th>-log A</th>
<th>Graphical Correction $A - 0.095$</th>
<th>log $(A - 0.095)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.549</td>
<td>0.260</td>
<td>0.454</td>
<td>0.343</td>
</tr>
<tr>
<td>5</td>
<td>0.394</td>
<td>0.405</td>
<td>0.299</td>
<td>0.524</td>
</tr>
<tr>
<td>15</td>
<td>0.282</td>
<td>0.550</td>
<td>0.187</td>
<td>0.728</td>
</tr>
<tr>
<td>20</td>
<td>0.168</td>
<td>0.775</td>
<td>0.073</td>
<td>1.137</td>
</tr>
<tr>
<td>25</td>
<td>0.151</td>
<td>0.821</td>
<td>0.056</td>
<td>1.252</td>
</tr>
<tr>
<td>30</td>
<td>0.140</td>
<td>0.854</td>
<td>0.045</td>
<td>1.347</td>
</tr>
<tr>
<td>45</td>
<td>0.123</td>
<td>0.910</td>
<td>0.028</td>
<td>1.553</td>
</tr>
<tr>
<td>60</td>
<td>0.095</td>
<td>1.022</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>0.095</td>
<td>1.022</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

*Absorption (disappearance) of unsaturated NO$_2$ group at 305.0 nm.*
TABLE IX

SPECTRAL DATA OF o-METHOXY-8-METHYL-8-NITROSTYRENE
AFTER TWO HOURS IRRADIATION

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>*Absorption</th>
<th>-log A</th>
<th>Graphical Correction *A-0.043</th>
<th>log (A-0.043)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.509</td>
<td>0.293</td>
<td>0.466</td>
<td>0.332</td>
</tr>
<tr>
<td>5</td>
<td>0.328</td>
<td>0.484</td>
<td>0.285</td>
<td>0.545</td>
</tr>
<tr>
<td>10</td>
<td>0.210</td>
<td>0.678</td>
<td>0.167</td>
<td>0.777</td>
</tr>
<tr>
<td>15</td>
<td>0.185</td>
<td>0.733</td>
<td>0.142</td>
<td>0.848</td>
</tr>
<tr>
<td>20</td>
<td>0.169</td>
<td>0.772</td>
<td>0.126</td>
<td>0.900</td>
</tr>
<tr>
<td>25</td>
<td>0.150</td>
<td>0.824</td>
<td>0.107</td>
<td>0.971</td>
</tr>
<tr>
<td>30</td>
<td>0.140</td>
<td>0.854</td>
<td>0.097</td>
<td>1.013</td>
</tr>
<tr>
<td>45</td>
<td>0.097</td>
<td>1.013</td>
<td>0.054</td>
<td>1.268</td>
</tr>
<tr>
<td>60</td>
<td>0.061</td>
<td>1.215</td>
<td>0.018</td>
<td>1.745</td>
</tr>
<tr>
<td>90</td>
<td>0.045</td>
<td>1.347</td>
<td>0.002</td>
<td>2.70</td>
</tr>
<tr>
<td>120</td>
<td>0.043</td>
<td>1.367</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

*Absorption (disappearance) of unsaturated NO₂ group at 333.75 nm.
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>*Absorption</th>
<th>-log A</th>
<th>Graphical Correction *A-0.200</th>
<th>log (A-0.200)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.654</td>
<td>0.184</td>
<td>0.454</td>
<td>0.343</td>
</tr>
<tr>
<td>5</td>
<td>0.494</td>
<td>0.306</td>
<td>0.294</td>
<td>0.532</td>
</tr>
<tr>
<td>10</td>
<td>0.288</td>
<td>0.541</td>
<td>0.088</td>
<td>1.056</td>
</tr>
<tr>
<td>15</td>
<td>0.240</td>
<td>0.620</td>
<td>0.040</td>
<td>1.398</td>
</tr>
<tr>
<td>20</td>
<td>0.164</td>
<td>0.785</td>
<td>-0.036</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>0.203</td>
<td>0.693</td>
<td>0.003</td>
<td>2.523</td>
</tr>
<tr>
<td>30</td>
<td>0.192</td>
<td>0.717</td>
<td>-0.008</td>
<td>-</td>
</tr>
<tr>
<td>35</td>
<td>0.189</td>
<td>0.724</td>
<td>-0.011</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>0.197</td>
<td>0.706</td>
<td>-0.003</td>
<td>-</td>
</tr>
<tr>
<td>45</td>
<td>0.197</td>
<td>0.706</td>
<td>-0.003</td>
<td>-</td>
</tr>
<tr>
<td>60</td>
<td>0.194</td>
<td>0.712</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>120</td>
<td>0.200</td>
<td>0.699</td>
<td>0.00</td>
<td>-</td>
</tr>
</tbody>
</table>

*Absorption (disappearance) of unsaturated NO₂ group at 300 nm.
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>*Absorption</th>
<th>-log A</th>
<th>Graphical Correction</th>
<th>log (A-0.085)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.611</td>
<td>0.214</td>
<td>0.526</td>
<td>0.279</td>
</tr>
<tr>
<td>5</td>
<td>0.324</td>
<td>0.489</td>
<td>0.239</td>
<td>0.622</td>
</tr>
<tr>
<td>10</td>
<td>0.220</td>
<td>0.658</td>
<td>0.135</td>
<td>0.870</td>
</tr>
<tr>
<td>15</td>
<td>0.205</td>
<td>0.688</td>
<td>0.120</td>
<td>0.921</td>
</tr>
<tr>
<td>20</td>
<td>0.178</td>
<td>0.750</td>
<td>0.093</td>
<td>1.032</td>
</tr>
<tr>
<td>25</td>
<td>0.123</td>
<td>0.910</td>
<td>0.038</td>
<td>1.420</td>
</tr>
<tr>
<td>30</td>
<td>0.105</td>
<td>0.979</td>
<td>0.020</td>
<td>1.699</td>
</tr>
<tr>
<td>60</td>
<td>0.095</td>
<td>1.022</td>
<td>0.010</td>
<td>2.000</td>
</tr>
<tr>
<td>100</td>
<td>0.085</td>
<td>1.071</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

*Absorption (disappearance) of unsaturated NO₂ group at 298.75 nm.
TABLE XII
THE SPECIFIC RATE CONSTANT AND HALF-LIFE FOR
THE REARRANGEMENT OF THE DERIVATIVES OF
8-METHYL-8-NITROSTYRENE

<table>
<thead>
<tr>
<th>No.</th>
<th>R</th>
<th>Rate Constant (x10^{-2} min^{-1})</th>
<th>Half-life (min) log A vs time</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2-CH_{3}</td>
<td>6.89</td>
<td>10.10</td>
</tr>
<tr>
<td>II</td>
<td>2-CH_{2}O</td>
<td>6.06</td>
<td>11.40</td>
</tr>
<tr>
<td>III</td>
<td>3-CH_{3}O</td>
<td>15.80</td>
<td>4.40</td>
</tr>
<tr>
<td>IV</td>
<td>4-CF_{3}</td>
<td>10.90</td>
<td>6.36</td>
</tr>
</tbody>
</table>
Photochemistry of o-methyl-α-methyl-α-nitrostyrene in 95% undenatured ETOH under N₂ (Conc. = 3.5 x 10⁻³M)

<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>
</tr>
<tr>
<td>3</td>
<td>30</td>
</tr>
</tbody>
</table>
Photochemistry of o-methoxy-β-methyl-β-nitrostyrene in 95% undenatured EtOH under N₂ (Conc. = 3.5 x 10⁻³ M)

<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>5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>
Photochemistry of m-methoxy-8-methyl-8-nitrostyrene in 95% undenatured ethanol under N₂ (Conc. = 3.5 x 10⁻³ M)

<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>5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
</tr>
</tbody>
</table>
Photochemistry of p-trifluoromethyl-β-methyl-β-nitrostyrene in 95% undenatured ethanol under N₂ (Conc. = 3.5 x 10⁻³ M)

<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>5</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>
First order plot for the irradiation of o-methyl-β-methyl-β-nitrostyrene
First order plot for the irradiation of o-methoxy-β-methyl-β-nitrostyrene
**Figure VII**

-Log A vs Time (min)

First order plot for the irradiation of m-metnoxy-β-methyl-β-nitrostyrene
First order plot for the irradiation of p-trifluoromethyl-β-methyl-β-nitrostyrene
CHAPTER V
DISCUSSION

At the time this study was started, Pinhey and Rizzardo\textsuperscript{5} in 1973 and Tang\textsuperscript{6} in 1974 were the only people who had studied the substituent effect on the nitro-nitrite photo rearrangement. Pinhey and Rizzardo reported that whereas cis-a-nitrostilbene (XLVIII) was converted in high yield into a mixture of isomers of benzil monoxime (XLIX) on irradiation in acetone, cis-a, 4-dinitrostilbene (L) under similar conditions gave only 38\% of the a-isomer of 2-phenyl-2-hydroximino-4'-nitroacetophenone (LIII), (also 19\% benzaldehyde (XLII), 11\% p-nitrobenzoic acid (LII), and 6\% 5-phenyl-3-(p-nitrophenyl)-1,4,2-dioxazole (L)\textsuperscript{5} was isolated.) Tang irradiated p-CH\textsubscript{3}, p-CH\textsubscript{3}O, p-Cl, p-nitro and m-nitro-\beta-methyl-\beta-nitrostyrenes. The yields of corresponding oximes were almost quantitative (90-100\%) except in the cases of 1-(p-nitrophenyl)-1,2-propanedione-1-oxime (15\%) and 1-(m-nitrophenyl)-1,2-propanedione-1-oxime (19\%).\textsuperscript{6} No clear reason for the formation of low yields of 1-(p-nitrophenyl)-1,2-propanedione-1-oxime was given. It was suggested that the electron-releasing groups attached at \textit{para} position of the phenyl ring promoted the nitro-nitrite rearrangement and electron-withdrawing groups attached at the \textit{para} or \textit{meta} position of the phenyl ring inhibited this
rearrangement and gave some fragmentation products. The possibility of a competition between the aromatic nitro group attached at the para or meta position and the unsaturated \( \beta \)-nitro group during the irradiation was also suggested. There was no evidence in terms of Tang's data to show that the absorption of the nitro group on the phenyl ring was about 80% higher than the unsaturated nitro group at the wave length at which irradiation was carried out. Additional work was needed with a number of electron withdrawing groups and electron donating groups on the phenyl ring before any conclusion could be made for the effect of the substituents on the nitro-nitrite photorearrangement. Our initial interest was to study the substituent effect on the photorearrangement of the derivatives of \( \beta \)-methyl-\( \beta \)-nitrostyrene. \( \text{CH}_3\text{O}, \text{CH}_3, \text{m-CH}_3\text{O} \) and \( \text{p-CF}_3-\beta \)-methyl-\( \beta \)-nitrostyrene (compounds not previously reported) were planned to be prepared. The CF\(_3\) group (with the Hammett substituent constant \( \sigma (\sigma) \) of 0.54 at the para position) was chosen because it exerts an electron withdrawing effect almost as great as the NO\(_2\) group with the Hammett substituent constant \( \sigma (\sigma) \) of 0.78 at the para position but it is not capable of absorbing light at the wave length employed. The CH\(_3\) and CH\(_3\)O groups at the ortho position were chosen because these groups exert an electron donating effect at the ortho position. Moreover, the effect of substituents at the ortho position had not been previously studied.
A consideration of the nature of the aldehydes that were to be condensed with nitroethane led us to use the method of Gairaud and Lappin,\textsuperscript{13} and the method of Robertson\textsuperscript{14} for the synthesis of various styrenes. In using the method of Gairaud\textsuperscript{13} a solution of p-tolualdehyde (p-anisaldehyde or o-anisaldehyde or o-tolualdehyde), nitroalkane, ammonium acetate and glacial acetic was refluxed for three to twelve hours. The recrystallized yield after recrystallization of the various styrenes and their melting points are summarized in Table I. A reflux time of twelve hours in the case of m-methoxy-\(\beta\)-methyl-\(\beta\)-nitrostyrene gave a dark brown oil which could not be made to crystallize. The most satisfactory procedure for the synthesis of o-methyl, o-methoxy, m-methoxy and p-trifluoromethyl-\(\beta\)-methyl-\(\beta\)-nitrostyrene was found to be the method of Robertson.\textsuperscript{14} A Schiff's base was prepared by refluxing a solution of o-tolualdehyde (o-anisaldehyde or m-anisaldehyde or p-trifluoromethylbenzaldehyde), n-butylamine and benzene in a boiling flask that was attached to a water separator (Dean and Stark trap) until the theoretical amount of water was collected. The solvent was then removed by distillation. This crude Schiff's base was then added directly to a solution of nitroethane and glacial acetic acid. The homogeneous mixture was refluxed under nitrogen gas for three to five hours and then poured into ice-water. The recrystallized yield of the various styrenes (using Robertson's method) and their melting points are summarized in Table II. The mechanism of this reaction can be described as follows:
2) \[
\text{CHNHCH}_4\text{H}_9 - \text{H}_2\text{O} \rightarrow \text{CH} = \text{NC}_4\text{H}_9
\]

3) \[
\text{C}_2\text{H}_5\text{N}:\text{O} + \text{CH}_3\text{COOH} \rightarrow \text{C}_2\text{H}_5\text{N}:\text{O} + \text{CH}_3\text{COO}^-
\]

4) \[
\text{C}_2\text{H}_5\text{N}:\text{O}^- + \text{CH}_3\text{COO}^- \rightarrow \text{CH}_3\text{CH}=\text{N}^-\text{OH}
\]

5) \[
\text{CH}=\text{NC}_4\text{H}_9 + \text{CH}_3\text{CH}=\text{N}^-\text{OH} \rightarrow \text{CHCHCHCH}_3
\]

6) \[
\text{CHCHCHCH}_3 \rightarrow \text{H}_2\text{NC}_4\text{H}_9 + \text{CH}=\text{CCH}_3
\]

7) \[
\text{H}_2\text{NC}_4\text{H}_9 + \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- \text{H}_3\text{NC}_4\text{H}_9
\]

8) \[
\text{CH}=\text{CCH}_3 + \text{C}_2\text{H}_5\text{NO}_2 \xrightarrow{\text{H}_2\text{NC}_4\text{H}_9} \text{CH}_3\text{CHNO}_2
\]

\[
\text{CH}_3\text{CHNO}_2 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{CHNO}_2
\]

\[
\text{CH}_3\text{CHNO}_2 \rightarrow \text{CH}_3\text{CH} = \text{NOH}
\]
In considering the above reaction by using the Robertson method\textsuperscript{14} a distinct improvement is made by elimination of water formed in step 2 and by tying up the basic amine formed in step 6, thus excluding by-product formation.

Ordinary preparations of the derivatives of 1-phenyl-1,2-propanedione-1-oxime require long reaction times and low yields are encountered in addition to their being fairly complex.\textsuperscript{25,26} The photochemical method of Tang\textsuperscript{6} for the synthesis of the derivatives of 1-phenyl-1,2-propanedione-1-oxime has been used by irradiation of the corresponding styrene in aqueous ethanol under nitrogen gas. Upon irradiation the greenish color of the solution of the derivatives of 8-methyl-8-nitrostyrene either faded away or became lemon yellow. In the case of m-methoxy-8-methyl-8-nitrostyrene a very dark color was observed after the irradiation. In each case irradiation was stopped after three hours and the solvent was removed under reduced pressure. The concentrate was recrystallized from a 50:50 solution of benzene
and ethanol and then recrystallized several times from ethanol. Higher melting points than those previously reported\textsuperscript{6} were obtained in the case of 1-(p-methyl-phenyl) and 1-(p-methoxy-phenyl)-1,2-propanedione-1-oxime. The recrystallized yields and the melting points of the various oximes are given in table III.

In order to study the substituent effect on the rearrangement the styrenes were irradiated for two hours in 95% ethanol under nitrogen gas with a pyrex filter. The vapor phase chromatographic analysis (using the method of Rosie and Grob\textsuperscript{23}) showed the yield of 1-(o-methylphenyl)-1,2-propanedione-1-oxime to be 99.10%, the yield of 1-(o-methoxyphenyl)-1,2-propanedione-1-oxime 99.75%, 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime 88.06% and 1-(p-trifluoromethylphenyl)-1,2-propanedione-1-oxime 86.75% (table VII). These results indicate that there is a rather small substituent effect on the rearrangement of the derivatives of 8-methyl-8-nitrostyrene. Electron donating groups attached at the ortho position of the phenyl ring promoted the nitro-nitrite rearrangement and electron-withdrawing groups attached at the para or meta position of the phenyl ring inhibited this rearrangement and gave some fragmentation products. The value of the substituent constants of $\sigma$ (sigma) for the trifluoromethyl group at the para position is 0.54 and that of the nitro group at the para position is 0.78. If the reason for the low yields of 1-(p-nitrophenyl)-1,2-propanedione-1-oxime (15%) and 1-(m-nitrophenyl)-1,2-propanedione-1-oxime (19%) in the
work of Tang⁶ and the low yields of cis-α, 4-dinitrostilbene (38%) as reported by Pinhey⁵ were to be attributed merely due to the electron-withdrawing effect of the nitro group, then it would have been logical to expect a much lower yield for the formation of 1-(p-trifluoromethylphenyl)-1,2-propanedione-1-oxime. However, the VPC yield of 86.75% of 1-(p-trifluoromethylphenyl)-1,2-propanedione-1-oxime clearly indicates that when the nitro group is attached at the phenyl ring (even though its electron-withdrawing power does effect the photorearrangement of nitro-nitrite to a small extent) the vast lowering of the yield of oxime and the fragmentation to aldehydes is caused by factors other than the electron-withdrawing effect of the nitro group at the phenyl ring.

Since the sigma (σ) value of -NO₂ group is in the same order as that of -CF₃ group and -NO₂ group is capable of absorbing light at the wave length employed while -CF₃ is not able to absorb light at this wave length we can conclude that there is a competition between the aromatic nitro group attached at the para or meta position and the unsaturated β-nitro group during the irradiation. This competition may well be the major cause for the lowering of the yield of the oximes with -NO₂ group attached at the phenyl ring. This conclusion supports the suggestion of Tang⁶ which predicted a possible competition between the -NO₂ group on the phenyl ring with that at the unsaturated double bond.

In order to obtain the order of the reactions and their half-lives, the progress of the reaction was followed by recording the ultraviolet spectrum as shown in fig I to IV.
Since a number of other groups are found to absorb light at or near the oxime band in the UV, it was experimentally easier to follow the disappearance of the unsaturated nitro group. The spectral data for the derivatives of $\beta$-methyl-$\beta$-nitrostyrene as summarized in tables VIII to XI suggest that the unsaturated nitro group was disappearing with increasing irradiation time. When log $A$ was plotted against time in each case (fig V to VIII) an initially straight line with the negative slope was obtained, suggesting that the disappearance for all the derivatives of $\beta$-methyl-$\beta$-nitrostyrene was initially a first order reaction. The half lives were calculated. There was no particular order for the half lives obtained (table XII). However, they were in the same magnitude as the half lives of styrenes irradiated by Tang$^6$ except in the case of $-\text{NO}_2$ group, again suggesting a competition between the $-\text{NO}_2$ on the phenyl ring and $-\text{NO}_2$ at the unsaturated double bond.

Recently Matsuura and co-workers$^3$ reported that there was no solvent dependency on the product ratio (aldehyde/oxime) for irradiation of nitrostyrenes. In order to examine this proposal we irradiated $m$-methoxy-$\beta$-methyl-$\beta$-nitrostyrene in benzene and $o$-methyl-$\beta$-methyl-$\beta$-nitrostyrene in cyclohexane. In each case irradiation using a pyrex filter was done under nitrogen flush for two hours. The VPC analysis for the yield of corresponding oximes indicated 65.68% of the yield of 1-($m$-methoxyphenyl$-$)-1,2-propanedione-1-oxime in benzene (compared to its yield of 88.06% in ethanol), and a 48.58% yield of 1-($o$-methylphenyl$-$)-1,2-propanedion-1-oxime in cyclohexane compared to its yield of 99.10% in ethanol. This
difference in photorearrangement due to the different solvents used clearly indicates that there is a solvent effect on the photorearrangement of styrenes as proposed by Chen.\(^4\)

Matsuura has also recently investigated the photochemical reactions of a series of substituted (E)-8-methyl-8-nitrostyrenes and proposed that nitro-nitrite rearrangement leading to the formation of the oximes and the intermolecular cycloaddition leading to the formation of the aldehydes are taking place competitively from different excited states.\(^3\) We have proposed the following mechanism for the breakdown of styrenes to aldehydes and their rearrangement to oximes. This mechanism unifies and includes ideas proposed by Chapman\(^2\), Pinhey\(^5\), and Matsuura.\(^3\)

\[
\text{III} \quad \text{Aldehyde} \quad \text{IV} \quad \text{Acid}
\]

\[
\text{III} \quad \text{III} \quad \text{IV}
\]
Irradiation of the \( \beta \)-methyl-\( \beta \)-nitrostyrene or its derivative (XXIII) gives an (n to \( \pi^* \)) exited state (LIV) (singlet or triplet). It is possible for the oxygen in the exited state to form a bond with either the \( \alpha \)-carbon or the \( \beta \)-carbon of the double bond. Formation of a bond between the oxygen and \( \alpha \)-carbon forms N-oxide ring (LIII) proposed by Pinhey and Rizzardo\(^5\) leading to the break down to benzaldehyde and the corresponding acid. Formation of a bond between the oxygen
of the exited state with the β-carbon forms an oxazidine ring (XXXII) proposed by Chapman\(^2\) which collapses to nitrite and leads to the formation of oximes. From the results of our work we have found that electron-withdrawing substituents such as \(-\text{CF}_3\) group in the case of \(\text{p-trifluoromethyl-β-methyl-β-nitrostyrene}\) or \(\text{m-CH}_3\text{O}\) in the case of \(\text{m-methoxy-β-methyl-β-nitrostyrene}\), tend to promote the formation of a bond between oxygen and α-carbon (in the exited state (LIV)) forming a N-oxide ring (LIII) which leads to break-down to aldehyde.

Electron donating substituents such as \(-\text{CH}_3\) attached at ortho position of the phenyl ring promote the formation of a bond between oxygen and β-carbon (in the exited state (LIV)) forming an oxazidine ring (XXXII) which collapses to nitrite and leads to the formation of oximes. This conclusion is in agreement with results of the work of Pinhey and Rizzardo\(^5\), of Tang\(^6\) and of Matsuura.\(^3\)
CHAPTER VI
SUMMARY

Our initial interest was to study the substituent effect on the photorearrangement of the derivatives of \( \beta \)-methyl-\( \beta \)-nitrostyrene. \( \text{o}-\text{CH}_3 \), \( \text{o}-\text{CH}_3\text{O} \), \( \text{m}-\text{CH}_3\text{O} \) and \( \text{p}-\text{CF}_3\)-\( \beta \)-methyl-\( \beta \)-nitrostyrene (compounds not previously reported) were synthesized using the method of Lappin\(^{13}\) and Robertson.\(^{14}\) These styrenes were irradiated in various solvents under nitrogen gas for two hours using the method of Tang.\(^{6}\) The yield of corresponding oximes varied from 95 to 100\% in aqueous ethanol. This variation in yield of the oximes was attributed to the effect of the substituent on the phenyl rings of the corresponding styrenes. Electron donating substituents attached at the ortho position of phenyl ring promoted the nitro-nitrite rearrangement and electron-withdrawing groups attached at the para or meta position of the phenyl ring inhibited this rearrangement and gave some fragmentation products. The results were compared to those of Pinhey\(^{5}\), Tang\(^{6}\) and Matsuura.\(^{3}\) In the mechanism which we have proposed it is suggested that the irradiation of \( \beta \)-methyl-\( \beta \)-nitrostyrene or its derivatives gives an \((n \text{ to } \pi^*)\) excited state \((\text{LIV})\) (singlet or triplet). Electron donating substituents at the phenyl ring tend to promote the oxygen in the excited
state (LIV) to form a bond with the β-carbon of the double bond. This leads to the formation of an oxazidine ring (XXVII) proposed by Chapman\(^2\) which collapses to nitrite and leads to the formation of oxime. Electron withdrawing substituents at the phenyl ring tend to promote the oxygen in the excited state (LIV) to form a bond with the β-carbon of the double bond. This leads to the formation of a N-oxide ring (LIII) proposed by Pinhey\(^5\) which breaks down to benzoaldehyde and the corresponding acid.

The effect of solvents on the irradiation of the derivatives of β-methyl-β-nitrostyrene was studied. The VPC yield of 1-(m-methoxyphenyl)-1,2-propanedione-1-oxime was 21% lower when benzene was used instead of aqueous ethanol as the irradiation solvent. Also, the yield of 1-(o-methyl-phenyl)-1,2-propanedione-1-oxime was doubled when aqueous ethanol was used instead of cyclohexane. Contrary to the suggestion of Matsuura\(^3\) these results clearly indicate that there is a solvent effect on the photorearrangement of styrenes as proposed by Chen.\(^4\)
BIBLIOGRAPHY


7. B. Priebs, Ber., 16, 2591 (1883).


25. W. Borsche, Ber., 40, 737.