8-1-1975

An investigation of the isolation and properties of 10-phenyl-10-thiaanthracene and 10-phenyl-10-thiaanthracene-10-oxide

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AN INVESTIGATION OF THE ISOLATION
AND PROPERTIES OF 10-PHENYL-
10-THIAANTHRACENE AND 10-PHENYL-
10-THIAANTHRACENE-10-OXIDE

A THESIS
SUBMITTED TO THE FACULTY OF ATLANTA UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE

BY
STANLEY GANDHI SEAY

DEPARTMENT OF CHEMISTRY

ATLANTA, GEORGIA
AUGUST 1975
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INTRODUCTION

Since the preparation of 1,2,4,6-tetraphenylthiabenzene (1) was reported by G. Suld and C. C. Price,\textsuperscript{1} a controversy has existed about the nature of these compounds. Evidence reported by Price\textsuperscript{2} indicates that thiabenzenes are stable aromatic compounds. Contradictory evidence was reported by Hortmann, et.al.\textsuperscript{8}, who concluded that thiabenzenes were ylides. It was also reported by Mislow, et.al.\textsuperscript{9}, that thiabenzenes showed evidence of being oligomeric in nature, and that the structure of the thiabenzenes was undetermined.

![Chemical Structure](image)

More recently, two thianapthalenes: 2-phenyl-2-thianapthalene (2), and 1-phenyl-1-thianapthalene (3), and two thiaanthracenes: 10-phenyl-10-thiaanthracene (4), and 9,10-diphenyl-10-thiaanthracene (5) have been reported by C. C. Price, M. Hori, T. Parasaran, and M. Polk.\textsuperscript{2} In each case, the desired product was achieved by the reaction of the corresponding perchlorate salt with excess phenyllithium under nitrogen.
Based chiefly on the dipole moments, the reactivity towards aromatic substitution reactions, and the nuclear magnetic resonance spectra,\textsuperscript{2} these compounds were presumed to be aromatic. The dipole moments were determined to be between 1.5 to 1.9 D.\textsuperscript{2} These dipole moments were determined by: measuring the molecular refractivity, using a General Radio
Company frequency capacitance bridge, oscillator and null detector to measure the dielectric constant, using a Pulfrich Refractometer to measure the corresponding refractive indices, and applying the Halverstadt-Kumler equation. These dipole moments were found to be quite small when compared to the dipole moments for two known ylides, 9-dimethylsulfonylfluorenylid (6,6,2D) and triphenylphosphonio cyclopentadienylid (7,7,0D).

The nuclear magnetic resonance spectra of (2,3,4, and 5) showed only aromatic type hydrogens, and coupled with the other information, this was considered as strong evidence for the aromatic nature of these thiabenzenes, thianaphthalenes, and thiaanthracenes.

A low dipole moment of 0.88 Debye was reported for yet another thiabenzene, 1-phenylthiabenzene (8), more recently by M. Polk, M. Siskin and C. C. Price. The low dipole moment and proton resonance only at 2.8 support the view of aromatic conjugation in this system.
Evidence contradicting the aromatic nature of the thiabenzenes has since been developed by A. G. Hortmann, et al. who reported the synthesis and analysis of 1-methyl-3,5-diphenylthiabenzenes (9) by treatment of 1-methyl-3,5-diphenyl-2H-thiinium tetrafluoroborate, with the anion of deuterated dimethyl sulfoxide, under nitrogen in an nmr tube.

The compound (9) was stable for at least one hour at thirty-five degrees centigrade since the original compound was obtained when the solution was treated with aqueous fluoroboric acid. Interpretation of the nuclear magnetic resonance spectrum and deuterium exchange results noted during the transient existence of the compound led
Hortmann to conclude that the product is not as stable as is normally attributed to aromatic compounds but that it probably exists in equilibrium with 1-methyl-3,5-diphenyl-2H-thiinium tetrafluoroborate. Hortmann also found that pronounced carbanionic character existed in the product. The accumulated evidence led him to conclude that, rather than aromatic, the compounds were quite ylidic in nature.

Other information indicating the controversial nature of these compounds has been provided by Senkler, Stackhouse, Maryanoff, and Mislow,9 who concluded that the thiabenzenes were oligomeric materials of undetermined structure. They reported that deprotonation of 10-alkyl- or 10-aryl-thioxanthylum salts (10) does not yield 10-thiaanthracene (11).9 These results were confirmed by Hori.10

\[
\begin{align*}
\text{(10)} & \\
a, \ R = \text{phenyl} & \\
b, \ R = 2,5-\text{Xylyl} & \\
c, \ R = \text{mesityl} & \\
d, \ R = \text{methyl} & \\
(6a-c, x=\text{ClO}_4; \ 6d, x=\text{BF}_4) & 
\end{align*}
\]
Since 10-phenyl-10-thiaanthracene was reported to be a stable species, the deprotonation reaction might be expected to proceed without rearrangement. Senkler, et.al. found, however, that work up of the compounds by the original techniques described by Hori\textsuperscript{2} did indeed produce the product described by Hori according to ultraviolet, Infrared, and \textsuperscript{1}H nuclear magnetic resonance spectra. However, they interpreted the \textsuperscript{1}H nmr spectra as being uncharacteristic of a simple monomeric species, because it showed a broad, featureless envelope absorption in the aromatic region. The \textsuperscript{13}C nmr spectrum was also uncharacteristic in the featureless manner. Elemental analysis of the compounds proved to be erratic although some samples actually did produce the expected analysis. All molecular weights were found to range from three to six times that expected of a monomeric species. Mass spectral analysis produced peaks with m/e values greater than the normal molecular weights expected for all the compounds analyzed. Therefore, they concluded that the nature of the compounds was undetermined and that the compounds were oligomeric in structure. They did mention that degradation of these materials did not provide evidence for their structure.\textsuperscript{9}

In a subsequent paper, the above researchers found that 1-phenyl-2-methyl-2-thianapthalene (12) rearranged when allowed to warm up to 40\textdegree to form 1-phenyl-1-methyl-2-thiochromene (13).\textsuperscript{9} This was interpreted as being
uncharacteristic of stable aromatic species, but more characteristic of ylides.

Hortmann, Harris, and Miles became interested in cleavage of the sulfoxide S-O bond as a means of converting 1-methyl-3,5-diphenylthiabenzene-1-oxide (14) directly to 1-methyl-3,5-diphenylthiabenzene (15) in order to study the shielding difference between a 1-phenyl- and a 1-methyl-substituted thiabenzene. They used several methods to produce the thiabenzene oxide. Addition of an acetylenic ketone (16) in dimethyl sulfoxide to dimethyloxosulfonium methylide (17) afforded the compound in good yield.

8
Attempts to produce the oxides of (18, b-d) were consistently erratic and the yields of 18e consistently low. Attempts to make the oxide by reacting 17 with acetylenic carbonyl compounds failed when dimethylacetylenedicarboxylate (19), propynal, and phenylpropynal were used. A final alternate route to these compounds involved the attempted transformations of cyclic ketooxosulfonium ylides (20). The products of these attempted transformations were oils and the work was discontinued.
Hortmann concluded from nuclear magnetic resonance data that the H-4 chemical shift of 14 was far enough upfield to suggest that no appreciable ring current existed in the thiabenzene-1-oxides. Hortmann also concluded that the nmr data, along with proton exchange data, suggested that the C-2, -4, and -6 positions of the S-ring bear relatively high electron density and are carbanionic in character. As a result of the above information, Hortmann suggested that thiabenzene-1-oxides may be viewed as cyclic sulfonium ylides.8

Price et.al.2 reported the preparation of 10-phenyl-10-thiaanthracene by the following sequence of reactions.
(2) \[
\begin{align*}
\text{H} & \quad \text{OH} \\
\text{[Chemical Structure]} & \quad \xrightarrow{\text{HClO}_4, \text{Et}_2\text{O}, -71^\circ} \\
\text{[Chemical Structure]} & \quad + \text{ClO}_4^-
\end{align*}
\]

(3) \[
\begin{align*}
\text{[Chemical Structure]} & \quad \xrightarrow{\text{Phenyllithium}, \text{N}_2 \text{ atm, Et}_2\text{O}, -71^\circ} \\
\text{[Chemical Structure]} & \quad + \text{ClO}_4^-
\end{align*}
\]
EXPERIMENTAL

Melting points were taken using a Thomas Hoover capillary point apparatus and are uncorrected.

Infrared spectra were taken on a Bausch and Lomb Spectronic 250 IR spectrophotometer or a Beckman IR5 infrared spectrophotometer in potassium bromide pellets. The instruments were calibrated at 4000 cm\(^{-1}\) and 5000 cm\(^{-1}\) respectively against the 6.238 \(\mu\) and 9.724 \(\mu\) bands of a polystyrene film. The nuclear magnetic resonance spectra were taken on a Varian Associates A-60A spectrometer. The nuclear magnetic resonance spectra were taken in deuterated chloroform containing 1% tetramethyilsilane or in carbon tetrachloride to which had been added a drop of tetramethyilsilane after the carbon tetrachloride solution of the compound to be tested had been put in an nmr tube. Chemical shifts are reported in parts per million (ppm) downfield from an internal reference. Ultraviolet spectra were taken using a Cary 17, UV-VIS-IR spectrophotometer. Ethanol was used as a solvent. The mass spectra were taken on a DuPont 21-490 mass spectrometer (70 ev).

The alumina chromatographic column contained Alcoa F-20 alumina. The column had an outside diameter of 2.7 cm. and a length of 48.5 cm.

Evaporation of solvents was accomplished using a Rinco Instruments Incorporated Rotary Evaporator, Model 1007-4.
Distillation in vacuo refers to evaporation using a Liebig, water cooled condenser connected to a vacuum pump.

Thioxanthen-9-ol (25).—A two liter, three necked flask, reflux condenser, and a pressure equalizer dropping funnel were cleaned, dried and assembled along with a mechanical stirrer, heating mantle, and a calcium chloride tube was attached to the condenser. Then 20g (0.0925 moles) of thioxanthen-9-one (Aldrich, 98%) were weighed and transferred to the assembled flask. Then 13.3g (0.3519 moles) of sodium borohydride added to 400 ml of methanol were put into the assembled, three necked flask along with the thioxanthen-9-one, and the mixture was stirred. The sodium borohydride solution was poured through a filling funnel into the dropping funnel and slowly added to the three-necked flask. After the initial reaction apparently had ceased, the mixture was refluxed. During reflux, the mixture turned orange-yellow, so a small amount of excess -0.5g/50ml- sodium borohydride in methanol was added and the reflux continued until a clear orange solution was produced (3 hrs.). The reflux was then discontinued and the solution allowed to cool, with stirring, to room temperature. The alcohol was isolated by precipitating it from water at a concentration of 50 ml of reaction mixture per liter of distilled water, and allowing the mixture to stand over the weekend. Filtration produced a very pale yellow solid material which, when recrystallized from petroleum ether (63-75%) produced a number of white crystalline needles: m.p. 101°; 104° lit²; the ir spectrum showed major peaks at 3190, 2650,
1500, 1440, 1200, 1130, 1090, 1048, 940, 748, 735, 689 and
642 cm\(^{-1}\); yield 83.5% (16.5g.).

**Thioxanthylum Perchlorate (26).--** First 9.0g (0.0042 moles) of thioxanthen-9-ol were dissolved in 100 ml of dry ether\(^2\) and suspended in a Dry Ice-acetone slush in a 250 ml flask along with a 250 ml flask containing 14 ml of 70% perchloric acid.\(^2\) The acid froze at -49° and the thioxanthen-9-ol was poured on top of the frozen acid. The interface between the two layers immediately became bright red. The flask was then removed from the slush and allowed to warm at room temperature,\(^2\) with occasional gentle shaking. At room temperature, a dark red precipitate was evident. The precipitate was filtered and recrystallized from hot 10% acetic anhydride in glacial acetic acid\(^1\) producing red crystals: m.p. 222°; the infrared spectrum had major peaks at 1578, 1543, 1490, 1385, 1260, 1109, 1082, 754 cm\(^{-1}\); yield 68.6% (crude); 43.6% (recrystallized).

**Synthesis of 10-phenyl-10-thiaanthracene (9).--** A 500 ml, three-necked flask was equipped with a fritted gas dispersion tube which had been inserted into a suitable rubber stopper. The dispersion tube was adjusted so that it would reach below the surface of the solvent. The opposite neck was sealed with a wired down serum cap and both joints were wrapped in paraffin paper. The assembly was then clamped to a ring stand over a pneumatic trough and a magnetic stirrer. The dispersion tube was connected by a rubber hose to a two valve manifold;
the other valve was connected by a rubber hose to a disposable pipette which was inserted into a bottle of phenyllithium (Ventron:Alfa Products; 70:30 Benzene-ether). A Dry Ice-acetone slush was put into the pneumatic trough so as to cover the flask up to the neck and 7.68% (0.0027 moles) of thioxanthylum perchlorate, and 200 ml of dry ether were then placed in the flask through the center neck. The neck was stoppered and sealed with paraffin paper. The phenyllithium and the flask assembly were then scrubbed, with stirring, for 10 minutes with nitrogen. Afterwards, 35 ml of 1 molar phenyllithium was injected into the flask, 10 ml at a time. The reaction mixture was stirred for 2½ hours. The reaction was then quenched by adding 200 ml of saturated aqueous ammonium chloride. A water layer and a dark, reddish brown ether layer, with a solid layer suspended at the interface were formed. The mixture was then filtered, transferred to a separatory funnel, and the water layer was removed. The ether was dried over anhydrous magnesium sulfate overnight, filtered and evaporated. The oily residue that remained was washed three times in pet ether (35-55°). A brown semisolid which formed was dissolved in 150 ml of anhydrous ether, and filtered through fluted filter paper to remove a light-brown precipitate. The filtrate was applied to an alumina column. The column was continually eluted with ether for 4 hours, and samples of 20 ml each were collected. Samples 6-13 were combined and evaporated, leaving a brown, amorphous residue:
m.p. 116-122°; the ir had major peaks at 3055, 1575, 1545, 750, and 700 cm⁻¹; the nmr produced one split peak between δ 7.1-7.7; the uv produced peaks at λ max 251 nm (log ε 2.93); and λ max 194 nm (log ε 3.29); the mass spectrum showed a large peak at 274 and a smaller peak at 290; yield 19.0% (1.4g).

**Isolation of 10-phenyl-10-thiaanthracene-10-oxide (23.)**

The light-brown crystalline substance that was produced as a by-product during the synthesis of 10-phenyl-10-thiaanthracene was recrystallized from acetic acid, which had been brought to a boil and removed from the heat. The by-product was then redissolved in the acetic acid, and the mixture was allowed to cool to room temperature. On suction filtration, white, crystalline dithioxanthyl was isolated. The acetic acid solution, which was a clear orange color, was then vacuum distilled to produce an orange residue. Attempts to dissolve the residue in pet ether (38-55°), and in anhydrous ether failed. However, a brown precipitate was formed in the anhydrous ether after bringing it to a boil in the flask containing the residue. The precipitate was transferred to another flask and allowed to cool to room temperature. Then the residue was dissolved in methanol. Evaporation of the methanol produced a brown crystalline substance: m.p. 120-122°; the ir spectrum showed major peaks at 1050, and 1225 cm⁻¹; the nmr spectrum showed a split peak between δ 7.2-7.8; uv analysis produced peaks at λ max 193 nm (log ε 1.30), and λ max 233 nm (log ε 1.38); the mass spectrum produced a small peak at 274 and a large peak at 290. The sample that was
isolated from ether produced the same mass spectrum as the sample that was isolated from methanol (parent peak m/e = 290).

Mass spectral data of the white, crystalline substance (dithioxanthyl) produced a peak at m/e = 394. The melting point was greater than 250°. These properties were consistent with those reported for dithioxanthyl by Hori.²
RESULTS AND DISCUSSION

Due to the amount of conflicting evidence that exists in the literature about the nature of the thiabenzenes, it was decided to make an attempt to accumulate evidence that would lend credence to the aromatic model for these compounds. The original problem was to decide how to make the compounds we considered to be aromatic. The "aromatic" thiabenzenes reported by Price were all made by reacting the thiapyrylium salts with phenyllithium. Attempts to produce these compounds by deprotonation did not produce products of interest. Therefore, it was decided to make 10-phenylthiaanthracene, because it was reported to be stable at room temperature, and to make it by the reaction of thioxanthyl perchlorate with phenyllithium because the product gave evidence of aromaticity. The starting material was chosen to be thioxanthen-9-one (21) because it was available from Aldrich Chemical Company at 98% purity.

In order to produce the thioxanthyl perchlorate which was desired, it was necessary to first reduce the thioxanthen-9-one to thioxanthen-9-ol. This was achieved easily by sodium borohydride reduction. The reduction proceeded smoothly and in high yield; however, since the product had been precipitated from water, it was quite wet. Since its melting point was 104-105°C, the product was dried overnight in an evacuated dessicator in order to give a reasonably good yield of
anhydrous product. Although the reaction proceeds smoothly, there is some difficulty in determining when the reaction is complete, because the starting material, which is light yellow, is soluble in hot methanol, and the product produces a light orange color when dissolved in the solvent. It was found, however, that a reflux time of three hours was sufficient to give an 83.5% yield compared to the 95% reported by Dr. Hori. Recrystallization of the product led to a loss of ca. 50%. However, thioxanthen-9-ol is stable at room temperature and can be stored and accumulated.

It was decided to prepare the perchlorate salt because the conditions for making it were simple and the time required to make it rather short. In reacting thioxanthen-9-ol with frozen 70% perchloric acid, it is only necessary to dissolve the thioxanthen-9-ol in anhydrous ether, pour the solution on top of the frozen acid and allow the acid to warm up to room temperature. Recrystallization of thioxanthylum perchlorate from glacial acetic acid proved to be rather difficult. The salt decomposes in boiling acetic acid, but if it is recrystallized from warm acid, it is not very clean so it must be recrystallized twice to produce a product with the properties reported by Hori. It is also difficult to produce similar yields from different recrystallizations. The final yield, after two recrystallizations, actually ranged from 14% to 43%. The temperature of the hot glacial acetic acid used to
recrystallize the thioxanthylum perchlorate, was not taken, so different recrystallizations may have been performed at different temperatures. Thioxanthylum perchlorate, however, is stable at room temperature and can be stored and accumulated.

The first preparation of 10-phenyl-10-thiaanthracene was performed in two stages. For one hour, the perchlorate was reacted with phenyllithium, with stirring, at -71°. Then the reaction vessel was removed from the slush bath and the reaction was allowed to continue with stirring for one hour. This method produced only a trace of the product, and it was decided to look, therefore, at the reaction more closely in an effort to choose conditions which might increase the yield. Hori had reported that one high molecular weight by-product was produced during the reaction.² He identified this compound as dithioxanthyl (22) m.w. = 394. It was known that biphenyl was also produced during the reaction.¹³ Considering that a high temperature reaction might increase the amount of high molecular weight by-products, and also considering that the highest reported yield for thiabenzenes was reported by Hori,² who ran the reaction at -71°, it was decided to run the reaction in a carbon dioxide-acetone slush and not to allow it to warm up but to quench it while still cold. These conditions produced a 19.0% yield of the desired product.
The nmr of 10-phenyl-10-thiaanthracene produced a split peak in the aromatic region. However, there was no envelope effect as previously reported. The mass spectrum produced only the parent m/e peak of the normal molecular weight which one would expect if 10-phenyl-10-thiaanthracene were monomeric. The small peak which appeared at m/e = 290 was not considered as evidence for the oligomeric nature of 10-phenyl-10-thiaanthracene, but as evidence for the presence of a trace of 10-phenyl-10-thiaanthracene-10-oxide, which was later isolated from the reaction mixture. 10-Phenyl-10-thiaanthracene proved to be very stable at room temperature in that it was kept for 7 months without any apparent change. If there was any oxidation at all, it was reflected in the small peak at m/e = 290 which appeared on the mass spectrum which was taken in March.

10-Phenyl-10-thiaanthracene-10-oxide (23) was precipitated from anhydrous ether as follows: the anhydrous ether which had
been used as solvent for the reaction of thioxanthylum perchlorate with phenyllithium was dried and evaporated; and the residual oil washed in petroleum ether (38-55°C) three times, then redissolved in anhydrous ether. The 10-phenyl-10-thiaanthracene remained dissolved in ether during the precipitation of 10-phenyl-10-thiaanthracene-10-oxide with petroleum ether.

![Structure](image)

Dithioxanthyl coprecipitated with 10-phenyl-10-thiaanthracene-10-oxide. These were separated by dissolving the two in hot glacial acetic acid, and allowing the acid to cool to room temperature. Dithioxanthyl precipitated at room temperature in the form of white crystals, but 10-phenyl-10-thiaanthracene-10-oxide remained dissolved in the acid. Distillation of the acid solution in vacuo produced a solid product having a brownish-orange color. Recrystallization from methanol produced what appeared to be a stable dark orange powder. The first indication that the compound was 10-phenyl-10-thiaanthracene-10-oxide was obtained from a mass spectrum of the compound which showed a parent peak of m/e = 290. An infrared spectrum of the compound was run as a
potassium bromide pellet because all other IR's of the synthesis products had been run using KBr. The IR spectrum showed a sulfoxide peak as indicated in the literature (1225 and 1050 cm\(^{-1}\)).\(^{15}\) It was assumed that the compound would be soluble in chloroform since it was soluble in methanol, so it was dissolved in deuterated chloroform (1% TMS) in order to run an nmr spectrum. The nmr spectrum showed only protons at \(\delta 7.1-7.7\) ppm. The peak was small and split, so the signal averager was applied, and after eight sweeps, a spectrum was obtained in which the peak could be clearly seen. In accordance with expectations, the nmr spectrum of 10-phenyl-10-thiaanthracene-10-oxide showed a peak which was centered at \(\delta 7.4\) in CDCl\(_3\) compared to the absorption centered at \(\delta 7.3\) in CDCl\(_3\) and CC\(_1\)\(_4\) for 10-phenyl-10-thiaanthracene. This would be expected due to the withdrawal of electron density by the oxygen atom. The deuterated chloroform was evaporated and a dark brown residue was obtained.

When it was attempted to take the melting point of 10-phenyl-10-thiaanthracene-10-oxide, it was found to soften at 70\(^\circ\)C, then turn light orange and finally melt at 120-122\(^\circ\)C. When the temperature reached 120\(^\circ\)C the compound turned dark again. Comparison of the uv spectra of the two compounds revealed that where 10-phenyl-10-thiaanthracene produced a peak at \(\lambda\) max = 251, 10-phenyl-10-thiaanthracene-10-oxide produced a similar peak at \(\lambda\) max = 233.
CONCLUSIONS

10-Phenyl-10-thiaanthracene may be produced by the reaction of thioxanthylium perchlorate with phenyllithium.

The nmr spectrum of this compound supports the aromatic model of its structure in that there was a broad peak only in the aromatic region with no peaks in the olefinic region. A peak in the olefinic region would have favored the ylide model for this compound (24):

![Chemical Structure](image)

If H⁹ appeared in the region in which olefinic protons normally appear, the nmr spectrum would favor the above model.

10-Phenyl-10-thiaanthracene is stable at room temperature for a long period of time. This type of stability is characteristic of most aromatic compounds.

Mass spectral analysis of 10-phenyl-10-thiaanthracene indicated that the compound is not oligomeric, but a monomeric species. One would expect that, if the compound were oligomeric, a peak would appear in its mass spectrum with an m/e value of at least twice the nominal molecular weight.
of the structure.

10-Phenyl-10-thiaanthracene-10-oxide also exhibits aromatic properties. The shift in the uv spectrum of 10-phenyl-10-thiaanthracene-10-oxide long wavelength absorption from $\lambda_{\text{max}} = 251$ to $\lambda_{\text{max}} = 233$ indicates a decrease in conjugation due to the bonding of the sulfur nonbonded electrons to the oxygen atom of the oxide. The shift in the uv absorption from $\lambda_{\text{max}} = 251$ for 10-phenyl-10-thiaanthracene to $\lambda_{\text{max}} = 233$ for 10-phenyl-10-thiaanthracene-10-oxide supports the aromatic model of 10-phenyl-10-thiaanthracene.
REFERENCES


ACKNOWLEDGEMENTS

The author wishes to thank Dr. Malcolm Polk, research advisor, for invaluable assistance during the entire research project, and especially for being available for consultation at inconvenient times. A special thanks to Dr. Thomas W. Cole, Jr. for the mass spectral data and for assistance with nmr spectra; and also to Dr. G. Scott Owen for instructions in running uv spectra. I would also like to thank fellow students Carl Barclay for assisting with nmr spectra, Ben Dias for assisting with uv spectra, and Joseph Kwabbi for assisting with uv spectra. Thanks to co-worker Jimmie Smith for help in many things during the entire project. To my friends not mentioned here, who have helped in many ways, I also offer my thanks. Finally, I wish to thank my wife for the many sacrifices she has had to make.