Halogenated Helicenes

Richard Wilbert Heiden

*Union College - Schenectady, NY*

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HALOGENATED HELICENES

by

Richard Wilbert, Heiden

Senior Thesis Submitted in Partial Fulfillment of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY
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This Thesis
Submitted by
Richard A. Heiden

to the
Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of
Bachelor of Science with a Major in Chemistry

is approved by

William B. Martin, Jr.
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INTRODUCTION

Literature references are an integral part of any research project. Without them one may find himself doing unnecessary work refining procedures already perfected. Unfortunately, it sometimes happens that even with appropriate sources the information is vague, or void of miniscule but important facts.

Ostensibly, scientists are pledged to reveal the whole truth. It is sad commentary on one's integrity to find his publication no more than a riddle containing half the information necessary for reproduction of the work. Even worse, however, are the periodicals which condone this practice for the sake of brevity. Truly scientists must communicate, or needless repetition combined with rising costs of research will inhibit progress.

In this study inadequate references were encountered frequently and caused me much unwarranted consternation. Thus, the following account of a year's work toward the synthesis of halohelicenes attempts to rectify this problem for the researcher fortunate to continue work on this and related subjects.
ABSTRACT

Attempts at synthesizing certain halohelicenes for studies in the following areas are described:

1) the testing of a new method of resolving optical isomers mechanically

2) electron spin resonance (ESR)

Since the purpose of the study was twofold, the decision to synthesize monochloro derivatives of hexahelicene was based on the time element and the comparative ease in which these particular compounds were thought to have been brought about (i.e. in direct comparison to polyhalo and higher order helicenes).

In addition to the traditional historical, theoretical, and experimental sections, an appendix containing a few suggestions relative to helicene research is included.

Despite time considerations the final step in our reaction procedure has not been reached.
HISTORICAL

In 1955 Newman's interests were centered on carcinogenic compounds and highly strained ring systems. Therefore, he very appropriately chose to endeavor the synthesis of a helical type system made up entirely of benzene rings.

The idea was probably not new, for many involved in cancer research were engrossed in the carcinogenic properties of benzo [6] phenanthrene analogues. But because of the vast intramolecular interactions and highly strained geometry, most thought phenanthro [3,4-~] phenanthrene, more commonly known as hexahelicene or [6] -helicene, to be extremely difficult and costly to make.

Newman's skeptics were correct on their assumptions, but following several unsuccessful attempts at dehydrogenation of the tetrahydro derivative (I) using palladium catalysts, the product was finally achieved via dissolution of (I) in benzene over 5% rhodium on alumina at 300° under nitrogen, in a pyrex lined high pressure cylinder for twelve hours. Furthermore, resolution proceeded only with extreme difficulty, and in fact required a rather unique procedure.

However, Newman's frugal use of the product established many startling characteristics which later became subjects of study. Among his contributions were ultraviolet and nuclear magnetic resonance spectra, and \[\alpha_D^{20}\] values for...
HEXAHELICENE

\[ \text{M.P (++) 270°} \]
\[ (-) 231-233° \]
\[ (-) 265-267° \]

\[ [6] \text{- helicene.} \]

The UV spectrum was not unusual for a phenanthrene analogue. But surprisingly, to some, the NMR revealed that "there do not appear to be any sizeable effects due to the helical overlap of rings."\(^1\) This indicated that possibly the helix was strained enough to minimize \( \pi \) orbital overlap and \( H - \cdot H \) repulsions between terminal benzenoid rings. Thus, to a certain degree the tremendous torsional strain in helical aromatic systems had been confirmed.

The specific rotation was also measured and found to be a remarkable \( [\alpha]^{20}_{D} = 3750\degree \) for (+)hexahelicene. This corresponds to a molecular rotation \( \phi \) of 12400 \degree.\(^1\)

High costs coupled with a recessional economy thwarted further research in the late fifties. But with increased
government expenditures in the early sixties came renewed enthusiasm. The high \([\alpha_D^{20}]\) values interested some in the optical properties and resulted in the publication of ORD and CD spectra.\(^2\)

The new data, combined with the fact that \([6]\)-helicene is one of the few molecules owing its inherent dissymmetry to intramolecular interactions, enlivened many theoreticians. Indeed a publication in 1961 revealed that for a helical aromatic system one could theoretically predict the UV from the ORD, and vice versa.\(^3\) By 1963 quantum mechanical wave equations for a particle travelling on a helix had been derived. In the same publication simple HMO approximations were employed to calculate the approximate ORD spectrum of the hexahelicene.

But during the early sixties little had been done in attempting the synthesis of the next highest ordered helicene, benzo \([6]\)phenanthro \([3,4-2]\) phenanthrene. Indubitably this was due to the difficulties which Newman encountered. Truly, heptahelicene would be even more sterically hindered than its lower benzologue predecessor. Obviously a new approach was necessary.

Utilizing a technique developed by Wood and Mallory for the photoconversion of stilbenes to phenanthrene in the presence of oxygen and iodine,\(^5\) Flammang-Barbieux was able to isolate \([7]\)-helicene in 20% yield using the following procedure.\(^6\)
The disadvantage of Flammang's work was obvious. It was a dead end proposition. That is, through his procedure one could not attempt higher order helicenes without significant difficulty in producing the intermediate compounds necessary for the desired ethylene derivatives. A new approach was again necessary. However, the success in achieving this helicene along with improvements on Newman's method for \([6]\)-helicene (resulting in 80% yields) provided the necessary impetus for further study.

By 1968 Wynberg and Groen had isolated hexa and hepta heterohelicenes (sulfur as hetero atom) in seventy and forty percent yields, respectively. They again employed Wood's techniques for the final steps, but also used a series of Wittig reactions to form the desired ethylenes. The utility of Wittig reactions for benzo helicene synthesis was
recognized almost immediately.

In 1969 R.H. Martin applied Wynberg's method and devised a scheme whereby the higher ethylene derivatives could be produced through the reaction of \((2\text{-benzo }[c]\text{-phenanthryl})\) methyl-triphenylphosphonium bromide with the corresponding aldehyde under Wittig conditions. Using this phosphonium ylid enabled him to synthesize the ethylenes required for photocyclization into hexa, hepta, octa, nona, and tridecahelicene. A typical reaction scheme is shown below.

**FIGURE III**

\[
\begin{align*}
\text{II} & \quad \text{Wittig} \quad \text{hv/I}_2 \quad \text{heptahelicene} \quad \text{hexahelicene} \\
\text{II} & \quad \text{Wittig} \quad \text{hv/I}_2 \quad \text{octahelicene} \\
\text{II} & \quad \text{NaNH}_2 - \text{NH}_3 \quad \text{hv/I}_2 \quad \text{nonahelicene} \\
\text{II} & \quad \text{O}_2, \text{C}_6\text{H}_6 \quad \text{hv/I}_2 \quad \text{nonahelicene} \\
\text{II} & \quad \text{Wittig} \quad \text{hv/I}_2 \quad \text{tridecahelicene} \\
\text{II} & \quad \text{Wittig} \quad \text{hv/I}_2 \quad 4\text{-azahexahelicene} \\
\end{align*}
\]
FIGURE IV

TRIDECASELICENE OR
[13]-HELICENE
Since the photocyclization of 1,2 diarylethylenes can give rise to isomeric polycyclic aromatic systems, identification of the final product is often difficult. To assist in identification R.H. Martin has proposed a method of deuterium labelling. Through mass spectrometry the final product can be determined. In the same publication he announced the isolation of 7-bromohexahelicene in 67% yield.

FIGURE V
R.H. Martin has achieved a milestone in helicene synthesis by reducing drastically the number of intermediate steps. Without further revisions in Martin's procedure [13], helicene appears to be the upward extent of the helical staircase. However, since helicene exists despite size and strain, it seems likely that someday helicene (n>13) will be reported, along with numerous derivatives.
THEORY AND PURPOSE

Because of ring overlap the helicenes are, in a sense, analogous to the paracyclophephane series.

FIGURE VI

1,1 PARACYCLOPHANE

P. Gerson and W. B. Martin, Jr. have recently studied the effects of ring overlap in negatively charged paracyclophephane radicals using ESR.* Of significant value in their findings was that for \( n \leq 3 \) in \( n,n \) paracyclophephane delocalization of the unpaired electron occurs between the two benzene rings.\(^{13}\) Others have elucidated charge transfer utilizing ESR techniques on sandwich-like ferrocene derivatives.\(^{14}\) Therefore, ESR would reveal not only reactivities and electron densities, but also would provide an indication of the amount of electron transfer in their radical anions.

With current theory correlating carcinogenicity with:

*An explanation of ESR is beyond the scope of this paper. However, it should be recognized that it is an effective tool for determining electron densities at any particular carbon atom. For further insight and explanation one should consult: Pasto and Johnson, Organic Structure Determination, chapter six; Bersohn and Baird, An Introduction to Electron Paramagnetic Resonance.
abnormally high electron densities at certain carbon atoms, ESR may also afford valuable knowledge pertinent to the potential carcinogenic character of these compounds.

The main reason for our study and the ultimate factor in the decision to synthesize halo derivatives was, however, quite unrelated to ESR spectrometry considerations. W. B. Martin, Jr. has proposed a method whereby the mechanical separation of helical optical isomers exhibiting an electric dipole is possible.

As a typical example, consider 3-chlorohexahelicene.

**FIGURE VII**

An electric dipole results with Cl present. If one were to place A and B in a solution of small spherical molecules (possibly CCl₄) and then in an electric field, theoretically a large number of the helices in solution would align with the field. If the field were then made to rotate continuously around a cylinder containing the solution the helical molecule would also rotate following the field. In corkscrew fashion they would then move up or
down depending on whether they are left handed or right handed screw helices.

Each isomer would collect at opposite ends and therefore could be removed via syringe. The procedure is then repeated for further purification.
Because of the inherent ease in directly halogenating an unsubstituted aromatic system, it was thought that once a helicene were produced, halo substitution or addition would proceed without much difficulty. The position of the functional group was not important since the only obvious necessity was an adequate dipole to follow the electric field.

Since the structural backbone of the helicene is the phenanthrene nucleus, halo addition became a particularly attractive possibility. However, the difficulties Newman encountered in dehydrogenation were recognized and it was realized that dehydrohalogenation may also prove to be an arduous task. Therefore, addition proposals were discarded in favor of substitution using iron trichloride or aluminum trichloride as catalysts.

Flammang's synthesis of heptahelicene as outlined in Figure II provided the nucleus of a scheme to produce halo-helicene. The synthesis of 3-phenanthryl acetic acid chloride was based on a variation of Mosettig's procedure for 3-phenanthryl acetic acid. The revised outline is depicted below.
**FIGURE VIII**

Acetyl chloride
AlCl₃/nitrobenzene

**STEP I**

1. NaOCl
2. H⁺

**II**

**III**

LiAlH₄

**IV**

Br⁻

**V**

CN⁻

**VI**

1. H₂O
2. H⁺

**VII**

SOCl₂
While considering substitution, however, it was decided that because of the intricacies necessary for separation of polychloro derivatives of phenanthrene and the high probability of polyhalogenating a helicene, it seemed impractical to attempt a separation of geometrical isomers. Ironically, this belief necessitated the production of a symmetrical, nonambiguous halophenanthrene to react with 3-phenanthryl acetic acid chloride in step I. The first choice was 9,10-dichlorophenanthrene. However, it was discovered that if the two and seven positions were also occupied, by-products in the final photocyclization probably would be reduced to a minimum. It might also increase the yield in this step substantially. Literature revealed syntheses of both 9,10-dichlorophenanthrene and 2,7,9,10-tetrachlorophenanthrene. Unfortunately, it was obvious that both procedures would be very time consuming, thus neither was endeavored. A few other methods of producing desireable halophenanthrenes are mentioned in the Appendix.

FIGURE IX

3,5,6,8-tetrachloroheptahelicene
EXPERIMENTAL PROCEDURE

Purification of Phenanthrene

Two hundred grams of technical phenanthrene were dissolved in 1 1/3 liters of 95% ethanol on a heating unit. The hot solution was decanted from any remaining insoluble material and cooled. One hundred ninety-five gms. of the recrystallized product were then redissolved in 440 cc. of hot glacial acetic acid. To the boiling solution was added 14.3 cc. of an aqueous solution containing 12 gms. of chromic anhydride. Then 6 cc. of concentrated H₂SO₄ were added slowly and the solution refluxed for 15 minutes more.

After dilution (with water) to twice the original volume, the mixture cooled. It was then filtered and washed well with water. The semi-purified phenanthrene was then vacuum distilled, yielding a yellow oil which soon solidified. The material was recrystallized four times from 95% ethanol yielding 160 gms. of phenanthrene, M.P. 98-99°.
3-Acetylphenanthrene (STEP I)

Ten gms. of purified phenanthrene were dissolved in 30 cc. of nitrobenzene which had been dried over CaCl₂. 16.5 gms. of AlCl₃ were added in small portions to 80 cc. of dried nitrobenzene and resulted in an olive colored solution. The two solutions were combined and put in an ice bath for about thirty minutes (anhydrous conditions). Then, 6 gms. of freshly distilled acetyl chloride were added all at once to the cooled mixture. The solution was then left in the ice bath for another half hour and allowed to stand at room temperature overnight.

The standing solution was poured over a large amount of ice in a 2 l. beaker. It was then stirred while 10 cc. of concentrated HCl were added.

The reaction mixture was then steam distilled to remove nitrobenzene as much as possible. The distillation residue, a dark brown viscous mass, was mixed with ether and the insoluble portion (2-acetylphenanthrene) was discarded.

The ethereal solution extracted from the steam distillation residue was dried over sodium sulfate, and the ether removed via vacuum aspirator. The resulting dark brown oil solidified.

To remove tarry by-products it was necessary to place the crude product in a Soxhlet extraction apparatus. Using petroleum ether (B.P. 40°-60°) as solvent, the tarry material collected in the thimble and on the sides of the boiling flask.
After extraction and removal of the pet-ether by conventional distillation, Mosettig suggests the use of vacuum distillation. To vary from recommended procedure, recrystallization employing the Norit decolorizer was attempted. After several recrystallizations from methyl alcohol a yellow coloration still persisted. After vacuum sublimation, however, pure white crystals (needles) were isolated with a melting point of 72°. The literature value is also 72°.

UV in cyclohexane revealed a $\lambda_{\text{max}}$ at 252 $\text{mu}$ with shoulders at 213, 232 and 242 $\text{mu}$. Another band was located upfield with small peaks at 307 and 322 $\text{mu}$. This was similar to data obtained from the literature. An IR was taken and showed the characteristic C=O stretch at approximately 1531 cm$^{-1}$. NMR showed a large singlet at 165 Hz., and multiple aromatic peaks between 400 and 600 Hz, but the substitution pattern could not be determined from this complex entity.

In all, 100 gms. of phenanthrene were reacted to yield a total of 48 gms. of 3-acetylphenanthrene (yield - 40%).
3-Phenanthroic acid (STEP II)

Twenty grams of sodium hydroxide were dissolved in approximately 380 cc. of water. Chlorine gas was then bubbled into the solution. Complete displacement of hydrogen by chlorine in the hydroxide was assumed.

Five grams of ketone were added resulting in a suspension. This was then refluxed lightly for four hours with constant stirring. The solution was tested for Cl content with starch iodine paper. No chlorine was present so the reaction was stopped and the mixture left standing overnight.

The next day a white precipitate of the acid's sodium salt was found. Sufficient water was added to dissolve the salt, and the remaining ketone was shaken out with ether and the water phase was transferred to a beaker. Concentrated HCl was added slowly to the water solution until precipitation was complete. The fine white precipitate was collected via filtration, washed well with water, and then redissolved in glacial acetic acid and recrystallized. Three grams of white needles (M.P. 268°-269°) gave a yield of 59%.

IR revealed the presence of acidic hydrogens with a broad absorption between 3650 cm\(^{-1}\) and 2400 cm\(^{-1}\). A strong, sharp absorption occurred at 1685 cm\(^{-1}\) (C=O stretch). A broadened moderate doublet was present at 1275 cm\(^{-1}\) (C-O stretch), as well as a moderate singlet at 1410 cm\(^{-1}\). All of these are characteristic carboxylic absorptions.
Utilizing the same procedure with reactant amounts quadrupled, it was found that after four hours of light reflux no Cl was present. The solution stood overnight and a white precipitate was noted the next morning. However, large amounts of the ketone remained unreacted in yellow balls. Addition of acid and recrystallization afforded 5.3 gms. of white needles, M.P. 269°, (26% yield). An IR spectrum was identical to that obtained in the first attempt.

Calcium hypochlorite, in a mixture of calcium oxide, calcium hydroxide and calcium chloride, was used in the next attempt. The required amount was calculated from the assay value of 30% Ca(OCl)\(_2\) recorded on the reagent bottle. Three gm. samples of ketone were oxidized but a total of only 1.7 gms. (16%) of the acid were isolated. In one case, where reflux was prolonged, complete removal of the C=O stretch in the IR resulted, and phenanthrene was isolated. Iodine titration of the Ca(OCl)\(_2\) mixture proved that only 4% was Ca(OCl)\(_2\).

A ten gram sample of the ketone was oxidized using potassium hypoiodite. The KOI was formed by first dissolving iodine in potassium iodide solution and then adding KOH. The same procedure was followed and formation of iodoform was noted. The 4.3 gms. of final product was a 42% yield.
DISCUSSION

Step I proceeded with ease. However, many techniques were employed in purification and this required much time.

Step II, on the other hand, provided difficulties. Small samples of the 3-acetylphenanthrene could be converted to the acid with good yields using sodium hypochlorite. However, when amounts in excess of ten grams were reacted the haloform reaction was slow, yields were poor, and in one case a total removal of the C=O stretch in the IR was evident. Several different hypohalites were tested for their efficiency. The calcium salt, Ca(OCl)$_2$, proved the least efficient, but this was due partially to the contamination of the reagent. An iodine titration proved that there was only 4% OCl present. Sodium hypochlorite was somewhat more effective than potassium hypoiodite.

With only limited success in the synthesis of 3-phenanthroic acid, it became necessary to reexamine the reaction procedure. Obviously, a large part of the problem was due to the ketone's inability to dissolve in water. Different organic solvents were tried and dioxane-water mixtures looked promising when further developments relieved the necessity of using Flammang's procedure.

The enigma posed by the loss of ketone C=O stretch in the IR was particularly perplexing. Few speculative arguments can be presented and upheld by the data. However, the presence of impurities in the reagent Ca(OCl)$_2$ may have been significant. In the early 1900's (unfortunately
the source has been misplaced) a publication in connection with the synthesis of phenanthroic acids stated that the presence of calcium oxide may remove the carboxylic function with long periods of refluxing. With a significant amount of the oxide known to have been present in the "bleaching" powder, this possibility became more imminent, although there was no conclusive evidence.

The discovery of R.H. Martin's work caused a reevaluation of Flammang's procedures. Martin's efforts appeared simple and straightforward. The number of intermediate steps was cut substantially and with the production of the four-ringed ylid intermediate one could immediately proceed to higher helicenes. Additionally, labelling with a halogen could be accomplished in a number of ways.
EXPERIMENTAL II

R.H. Martin's procedures (Figure III) thus became the basis for further experimentation. The pathway to the intermediate ylid is described below. 12

FIGURE X

\[
\begin{align*}
\text{STEP I} & \quad \text{CH}_2\text{Br} + \phi_3\text{P} \xrightarrow{C_6H_6} \quad \Phi_3\text{CH}_2\text{Br} \\
\text{X=H or Br} & \quad \text{CHO} + \phi_3\text{P} \xrightarrow{\text{Li/MeOH}} \Phi_3\text{CHO} \\
& \quad \xrightarrow{\text{Wittig}} \Phi_3\text{CHO} \\
& \quad \xrightarrow{\text{hv/I}_2} \Phi_3\text{CHO} \\
& \quad \xrightarrow{1,\text{N.B.S/CCl}_4} \Phi_3\text{CHO} \\
& \quad \xrightarrow{2,\phi_3\text{P/xyylene}} \Phi_3\text{CHO}
\end{align*}
\]
Several methods of obtaining halohelicenes were suggested. One, devised by R.H. Martin, has been mentioned previously. It entails the production of 3-bromo-4-tolualdehyde. This is used in place of p-tolualdehyde in Step II. Other attempts at the synthesis of this compound were based on D.E. Pearson's swamping catalyst effect.

The ylid production and Wittig reactions were based on general procedures since no specific reference utilizing Wittig techniques for the desired diaryl ethene could be found.

Photocyclizations were based on Mallory's procedure already mentioned.

Unfortunately, Martin's work did not provide the necessary sources or details for his scheme, and caused considerable problems in producing the intermediates.
EXPERIMENTAL PROCEDURE

(2-Naphthyl)methyl-triphenylphosphonium bromide (I)

A

In a dry flask .01 moles (2.2 gms.) of 2-bromomethyl-napthalene (M.P. 52°-59°) were dissolved in 100 ml. of benzene. Then .01 moles of triphenylphosphine (M.P. 79°-81°) were dissolved in another 100 ml. benzene. The two solutions were combined and the resultant mixture refluxed lightly for three hours under anhydrous conditions. A chalky white solution resulted during the reflux. After filtration the fine white precipitate was washed thoroughly with benzene. After drying, a melting point was taken and found to be 250°-251°. The IR indicated a moderate peak at 2300 cm.\(^{-1}\) (P-C stretch) and the absence of a P=O absorption at approximately 1190 cm.\(^{-1}\). A strong, sharp peak occurred at 1420 cm.\(^{-1}\) and moderate peaks were evident at 1460 cm.\(^{-1}\), 1560 cm.\(^{-1}\), 2820 cm.\(^{-1}\) and 3000 cm.\(^{-1}\) (broadened). The product weighed 2.95 gms. and represented a 61% yield.

B

Fifty-nine grams of triphenylphosphine were added slowly to 500 ml. of benzene in a liter flask. Then 50 gms. of the 2-bromomethylnapthalene were added slowly until completely dissolved. The solution was stirred at room temperature for fifteen hours under anhydrous conditions. The reaction mixture was filtered and washed. Then the mother liquor was refluxed for six hours. The product collected
from the mother liquor was filtered and washed. A total of 102 gms. of the ylid were produced (93.5%). An IR was identical with that obtained from A.

In another reaction utilizing the same procedure 107 gms. of product were yielded (88%).
1-(2-Napthyl)-2-(p-tolyl)ethylene (STEP II)

A

Two and nine tenths grams of the ylid from step I were dissolved in 50 ml. of absolute methanol under anhydrous conditions. One gram of lithium was dissolved in another 50 ml. of absolute methanol and added all at once to the ylid solution (now under nitrogen atmosphere). The solution was mixed thoroughly for fifteen minutes and 0.55 gms. of p-tolualdehyde were added slowly. The reaction mixture was then refluxed for five hours. The formation of tiny white flakes of product was evident throughout the reflux. The product was filtered and washed with methanol. A total of 0.54 gms. (50%) of olefin was isolated (M.P. 181°-184°). After recrystallization from cyclohexane a melting point of 186° was recorded. An NMR spectra could not be taken because of the olefin's inability to dissolve in common solvents. An IR revealed the presence of a weak C=C stretch absorption at 1625 cm.⁻¹ and a strong absorption probably due to C-H bending at 965 cm.⁻¹. This absorption is characteristic of trans olefins. In addition, aromatic, olefinic and methyl C-H stretching was indicated in a broad, moderate sized band with multiple peaks between 3100 cm.⁻¹ and 2800 cm.⁻¹. Ultraviolet analysis showed a λ_max at 327 mµ with a shoulder at 340 mµ, a smaller peak at 288 mµ with shoulder at 278 mµ, and a still smaller peak at 245 mµ with an adjacent shoulder at 257 mµ. Comparison of the UV with the characteristic absorptions for trans stilbene reinforced our conclusions that this product was a similar olefin.
B

Ninety grams of the ylid were dissolved in 500 ml. absolute methanol with 4 grams of lithium in solution. The same conditions were maintained (anhydrous, N₂ atmosphere). The mixture was allowed to stand for half an hour and then 22.4 gms. of p-tolualdehyde were added. The reactants were constantly stirred while refluxing for 15 hours. The product weighed 18.6 grams, had a melting range of 183°-184°, and equalled a yield of 44%.
2-Methyl-benzo[c]phenanthrene (STEP III)

Five hundred seventy milligrams of olefin were dissolved in 450 ml of distilled cyclohexane solution. Thirty-three milligrams of iodine were then added and the entire solution transferred to a special photolysis reaction vessel. The vessel consisted of a pyrex well with a ground glass fitting for a quartz tube in which the UV lighting tube was placed.

After four hours the photolysis was stopped and the rose colored solution poured into a separatory funnel. The iodine was then removed by shaking the reaction mixture in the presence of thiosulfate solution. The resulting cyclohexane phase was yellow-brown.

The products were separated using column chromatography with alumina as adsorbent. The fractions were analyzed by UV to determine the products, and were then combined and the solution evaporated via the "Roto Vapo" vacuum aspiration techniques. An NMR revealed multiple aromatic peaks downfield and a large singlet due to the methyl substituent was located at 247 Hz. A 3.7:1 or 11.1:3 integration ratio resulted. UV revealed a $\lambda_{\text{max}}$ at 287 m$\mu$. Phenanthrene has a $\lambda_{\text{max}}$ at 253 m$\mu$ and thus the bathochromic shift to 287 m$\mu$ with the addition of one benzene ring is not unreasonable. The product formed crystals from cyclohexane-toluene, and melted at 80°-81° (Literature value = 82°). A total of 50 mgs. (9.8%) of product was isolated.

Three similar runs were tried with varying concentra-
tions of iodine and it was found that a reaction time of one hour and about 5 mg. of iodine was sufficient for the best run, which resulted in approximately 150 mg. (27% yield). These concentrations and reaction times are similar to those reported recently by Martin, enabling him to obtain this product in 80% yield.
Synthesis of 3-Bromo-4-tolualdehyde

Three unsuccessful attempts were made at producing this compound. However, in a fourth attempt some success was achieved.

Eighty and eight-tenths grams of p-tolualdehyde was poured into a pre-dried 1000 ml. three-neck flask fitted with a stainless steel stirrer. Then, 216 gms. of anhydrous aluminum chloride were added slowly making sure that the solution temperature did not rise over 80° (to prevent oxidation or loss of carbonyl function). The resulting mixture became extremely viscous and the electric motor driving the stirrer was considerably burdened. One hundred twenty-eight grams of bromine were added in an hour's time with considerable evolution of heat. The reaction mixture was stirred for several hours until no more HBr evolved, and then allowed to set overnight.

The crude product was scraped from the reaction vessel into a two liter beaker containing cracked ice and 100 ml. of concentrated HCl, and hand stirred vigorously. The dark colored oil was then extracted with ether, washed with water, and then washed with sodium bicarbonate solution. The ether was removed via aspirator.

After careful fractional distillation with nitrogen passing through the apparatus, the final product was isolated and recrystallized from hexane yielding six grams (4.5%) of white needles M. P. 40-41°.

NMR showed complex splitting patterns between 418 and
480 Hz. Singlets due to the aldehydic proton and methyl hydrogens were located at 614 and 155 Hz., respectively. Integration showed an approximate 3:3:1 ratio.

A"Varian A-60" spectrometer was used for all NMR spectra.
An Attempt at the Synthesis of
Chloromethyl-triphenylphosphonium chloride

Ten grams of triphenylphosphine were dissolved in an excess of dichloromethane. The resulting solution was refluxed for over fifteen hours. The excess solvent was removed by aspiration and the product was allowed to dry. The melting point was 83° and the IR was an exact replica of a spectrum for triphenylphosphine.
DISCUSSION II

The difficulties incurred in Martin's procedures were, to a large extent, due to inadequate references. Martin's publications were in *Tetrahedron Letters*, which must be famous for its brevity by now. Martin claims that yields in each of the steps were high (above 50%), but enough references or experimental procedures could not be found to enable one to reproduce his work directly.

It is felt that considerable increases in yield for step II would result if the mixture of ylid salt and methanol-lithium methoxide were allowed to stand at room temperature for another thirty minutes (under anhydrous, Nitrogen atmosphere). This would allow more time for formation of the resonance stabilized ylid intermediate which is largely responsible for the reaction with tolualdehyde.

Once the proper iodine concentration had been determined, half the problems encountered in step III had been solved. Much of the product was not separated and was therefore mixed with by-products. Fortunately, this situation can be ameliorated by further chromatographic separations.

The swamping catalyst effect described previously caused a considerable amount of trouble. The huge quantities of aluminum trichloride often made the reaction mixture so viscous that the paddle-shaped teflon stirrer was bent and rendered useless. The use of a stainless steel stirrer helped immensely, in that it was possible to finish
the reaction. An increased yield probably could be afforded through use of smaller amounts of reactants.

With only limited success in obtaining 3-bromo-4-tolu-aldehyde another method of halogenation was devised.

It was decided that the following scheme could provide a dihalo 2-methyl-benzo[c]phenanthrene.

FIGURE XI

Decolorization of a mixture of the olefin (from step II) and bromine in chloroform occurred readily, but the resultant product was insoluble in most common solvents, save methylene dichloride. Therefore, two dehydrohalogenations would have been arduous.

After careful consideration it was finally decided
that the desired ethylene could be procured through a reaction of the phosphonium ylid in step IV with the chlorobenzaldehyde. After photocyclization this would yield a chlorohexahelicene. Depending on whether ortho, meta, or para chlorobenzaldehyde were used, the following products would be formed.

FIGURE XII

4-chlorohexahelicene from o-chlorobenzaldehyde

2-chlorohexahelicene from p-chlorobenzaldehyde

3-chlorohexahelicene or 1-chlorohexahelicene from m-chlorobenzaldehyde
CONCLUSION

This thesis has paved the way for further work on the helicene series. To date, the chloroisomers of hexahelicene have not been produced. However, it is felt that with continued research a facile synthesis of these isomers is within reach.
APPENDIX

In this section are several suggestions pertinent to the development or improvement of procedures already mentioned. It is hoped that this will assist those interested in reproducing or furthering research on the helicene series. These suggestions are, however, purely speculative.

A. 9,10-dichlorophenanthrene

\[
\text{hv/}I_2
\]

B. 1,8-dichlorophenanthrene
C. 1,2,7,8,9,10-hexachlorophenanthrene

D. 3-phenanthryl acetic acid

1. Mg
2. CO
3. \( \text{H}^+ \)

\[ \text{CH}_2\text{COOH} \]
E. $[n]$-helicene

\[ + \]

\[ \text{Wittig} \]

\[ \text{hv/I}_2 \]

$[n]$ -helicene
REFERENCES

17. Sandquist, H.; Berichte, 51, 1521 (1918).