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# Toward a synthesis of acenaphth (1,2-a) acenaphth (1,2-a) acenaphthene

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TOWARD A SYNTHESIS OF  
ACENAPHTH(1,2-a)ACENAPHTH(1,2-a)ACENAPHTHENE

by

John Isaac Gerson *UC 1969*  
"

\* \* \* \* \*

Submitted in partial fulfillment  
of the requirements for  
Honors in the Department of Chemistry

UNION COLLEGE

May, 1969





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# ABSTRACT

GERSON, JOHN. Toward a Synthesis of Acenaphth(1,2-a)acenaphth(1,2-a)acenaphthene. Department of Chemistry, May, 1969.

The purpose of this project was to synthesize acenaphth(1,2-a)acenaphth(1,2-a)acenaphthene. The project originally followed Letsinger's preparation of a synthetic precursor called acenaphth(1,2-a)acenaphthylene, which was to be dibrominated, giving the cis-6b,12b derivative. This derivative was to be reacted with naphthalene to yield the desired product; but this route was abandoned when a necessary forerunner of Letsinger's hydrocarbon called 1,8-dibromonaphthalene was obtained in very low yield.

An alternate procedure leading to Letsinger's hydrocarbon, involving the Friedel-Crafts addition of 1,8-di(chloromethyl)naphthalene to naphthalene, was devised, and a synthetic precursor of the former compound called 1,8-dimethylolnaphthalene was obtained.

Three shorter Friedel-Crafts and related closures were attempted. First, acenaphthene was stirred with naphthalene in the presence of a catalytic amount of palladium-on-carbon. Second, acenaphthylene was stirred with naphthalene in cyclohexane in the presence of excess aluminum chloride. Third, the previous reaction was repeated with acenaphthylene which had been dibrominated. Gas chromatography showed no products were formed in the first two reactions, while the results for the third reaction were not definitive.



This Thesis

Submitted by

John L. Gibson

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.



### Acknowledgment

I wish to thank Dr. William B. Martin, Jr. of Union College for his inspiring aid on this project. His suggestions and continued encouragement were greatly appreciated.

John I. Gerson



## Table of Contents

Introduction	1-2
Historical	3-4
Experimental	5-16
Discussion	17-22
Conclusion	23
Figures	24-25
Appendix	26
Bibliography	27-28



## Introduction

The purpose of this project was to synthesize acenaphth-(1,2-a)acenaphth(1,2-a)acenaphthene (I on Figure 1.). The compound is expected to be of interest for a number of reasons. First, the dotted carbon-carbon bond in (I) is expected to be unusually long. A molecular model of (I) indicates that this bond would be as long as 2.3 or 2.4 Å, as compared to the usual bond length between carbon atoms of 1.20 to 1.55 Å (1). This molecular model assumes that, uniquely, all the carbon atoms in (I) are  $sp^2$  hybridized, an assumption that leads to bond angles favorable for the formation of the  $\sigma$  skeleton of (I).

Other areas of interest which can be explored once (I) is prepared depend upon its symmetrical properties. For instance, substitution even by three of the same functional groups, one on each of the three naphthalene rings, but relatively in different positions (i.e. 2, 3', 4'') should result in optical isomerism. This type of stereoisomerism would be more permanent than the related diphenyl optical isomerism of no single center of asymmetry, since the geometry of (I) does not permit racemization through rotation of the rings about a bond joining them as occurs in diphenyl optical isomers.

Electron spin resonance studies of the radical prepared from (I) would be interesting from the standpoint of showing if an electron can be delocalized over the entire molecule as might be predicted from the behavior of known radicals. Work done by Gerson and Martin (2) with diphenylmethane and



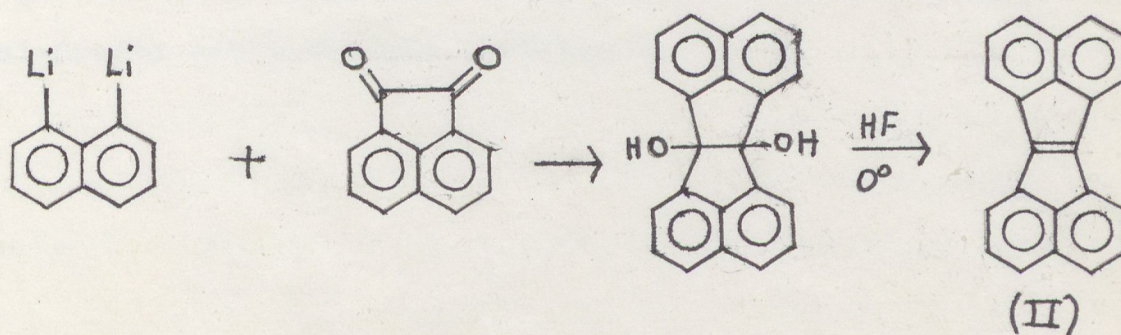
paracyclophanes (2.2-; or 3.3) indicates that electron delocalization would be expected over all three rings in (I). However, in the case of (I), the rings are not held parallel to each other, nor is there any relative motion of one naphthalene ring system with respect to another. Electron spin resonance studies of (I) would show the importance of ring mobility in determining electron delocalization.



### Historical

While the synthesis of (I) is not reported in the literature, the synthesis of a precursor, acenaphth(1,2-a)acenaphthylene (II), has been published by at least two independent investigators.

Letsinger (3) obtained (II) by means of the following reaction: condensation and subsequent hydrolysis of equimolar quantities of 1,8-dilithionaphthalene and acenaphthenequinone to yield the diol corresponding to (V). Formation of (II) from the diol involved, according to Letsinger, elimination of cis-hydroxyl groups. He accomplished this in a most interesting manner. He mixed 0.700 gm. of the diol with 15 ml. of anhydrous hydrofluoric acid in a copper vessel at 0° for 45 minutes. The material was extracted with benzene, washed with water, dried, and separated on an alumina column, using hexane-benzene mixtures as eluants. He obtained from the diol a 29% yield of (II), which was found to be a purple crystal with a melting point of 284-285°. Unfortunately, Letsinger does not postulate a mechanism for the reduction. The synthesis is shown below.





Agosta's (4) preparation of (II) is of less relevance to this paper, since it involved a series of complicated transannular reactions which he was investigating, making his synthesis longer. However, as will be shown later, he did make some observations concerning a part of his synthesis of (II) which are of significance for this project. Agosta's synthesis of (II) began with the synthesis of the corresponding diketone 1,8-(1',8')-naphthalyl-naphthalene (III). Agosta prepared (III) from the corresponding diol mentioned in Letsinger's reaction above. Agosta treated the diol with lead tetraacetate to produce oxidative cleavage of the diol, yielding (III).

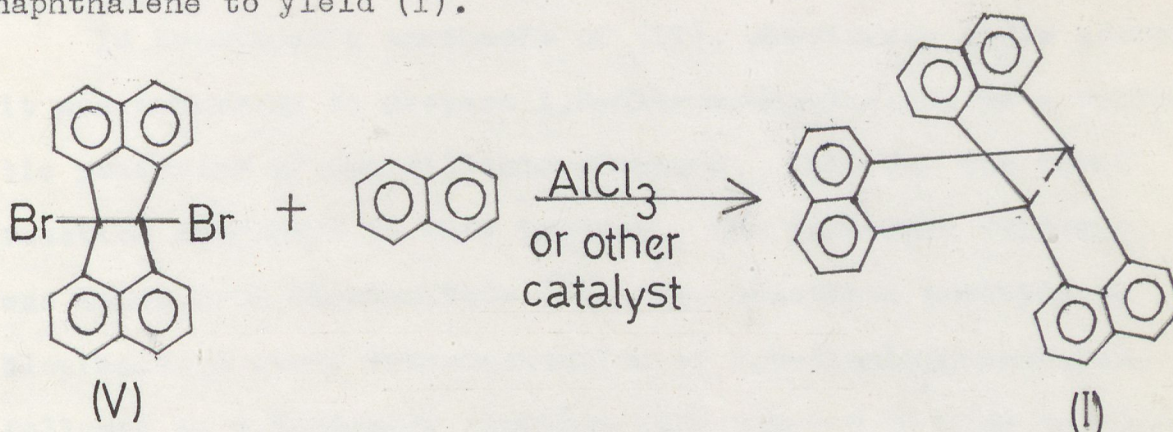
In searching for a more convenient route to (III), Agosta tried a number of Friedel-Crafts closures. They are described here since some related Friedel-Crafts reactions were attempted in connection with this project. The closures were attempted on the readily available 8-(1'-naphthoyl)-1-naphthoic acid (IV) and on its 2'-methoxy derivative. Agosta stated that all his attempts failed using both the treatment with phosphoric anhydride in hot toluene described by Knapp (5), and "a variety of other procedures," meaning presumably a variety of Friedel-Crafts catalysts and conditions.



## Experimental

### A. Plans

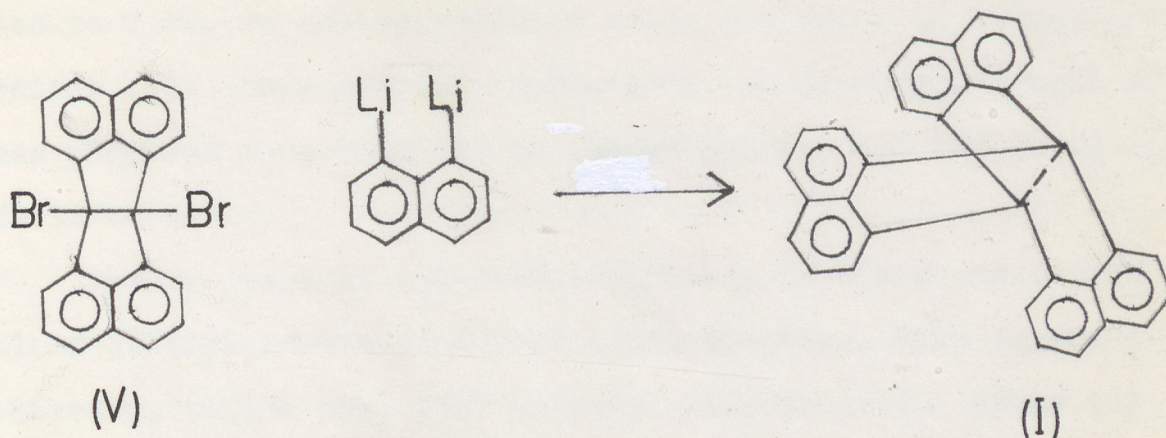
The original plan for the synthesis was to duplicate Letsinger's work up to the formation of (II). Once (II) was prepared, it was planned to dibrominate it to give (V). Letsinger (6) noted a 95% yield in this reaction, when he treated (II) with bromine in chloroform solution to yield "probably the cis-isomer." The high yield upon bromination showed a low degree of aromatic character of the double bond in (II). Compound (V) would then be reacted under Friedel-Crafts conditions with naphthalene to yield (I).



Although dialkylation might occur on only one ring of naphthalene, it was hoped that steric factors would favor 1,8 dialkylation.

An hypothesized alternative to the above reaction called for the condensation of (V) with 1,8-dilithionaphthalene to yield (I). The reaction is shown on the next page.

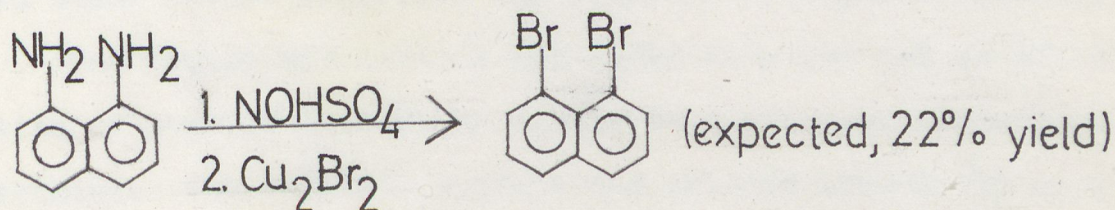




### B. Procedure

#### Reaction 1.

In Letsinger's synthesis of (II), previously cited above, it was necessary to prepare 1,8-dibromonaphthalene as a synthetic precursor of the dilithio compound. This was the first reaction attempted in this project. The procedure followed was taken from Klopfenstein (7). The reactions employed by Klopfenstein were: tetrazotization of 1,8-diaminonaphthalene followed by a Sandmeyer reaction with cuprous bromide to yield the desired dibromo compound.



The tetrazotizing agent used was not the familiar nitrous acid, but was nitrosylsulfuric acid. Klopfenstein was able to purchase this reagent, but in this project, it was prepared



using the ratio of 1 gm. of finely powdered sodium nitrite added to 7 ml. of cooled sulfuric acid, according to Hodgson and Walker (8). Approximately 0.264 mole of nitrosylsulfuric acid was prepared from 17.9 gm. of sodium nitrite and 125 ml. of sulfuric acid.

Twenty grams of 1,8-diaminonaphthalene dissolved in 160 ml. of glacial acetic acid were added dropwise, with constant stirring, to the cold (10°) nitrosylsulfuric acid. After 1.5 hours, when all of the 1,8-diaminonaphthalene had been added, the mixture was allowed to come to room temperature and was stirred for an additional hour.

Before the above addition, 16 gm. of cupric oxide, 200 ml. of 47-49% hydrobromic acid, 25.2 gm. of finely powdered copper turnings, and 120 ml. of water were added together, heated and stirred for 1.5 hours. City gas was bubbled through this mixture to remove any oxygen present, and the mixture was stoppered and allowed to stand overnight. A small aliquot of the colorless solution was allowed to oxidize in air. The deep red color formed suggested the presence of cuprous bromide.

The diazotized mixture was added to a hot (80 to 90°) solution of cuprous bromide at a rate that produced controlled frothing. The reaction mixture was stirred constantly by a mechanical stirrer. Addition was complete in about 30 minutes. The black mixture was then allowed to stand in the hood for two days.

The black slurry was next filtered with a Buchner funnel



and press-dried into a cake. The cake was once thoroughly mixed with 120 ml. of hot 95% ethanol and filtered. The cake was washed once again with ethanol and once with benzene. The total volume of filtrates (about 400 ml.) were combined. Rectangular blue crystals were noted within the black cake, and some of these were saved. They were originally blue in color, but upon heating on a Fisher melting point apparatus, became first white at 85° and then black at 210°. They failed to melt, even when a temperature of 285° was attained. The combined filtrates were evaporated to dryness on a Buechler rotary flash-evaporator. The black residue was dissolved in 160 ml. of benzene and was washed once with 160 ml. of 10% sodium carbonate and once with water. The sodium carbonate wash formed a black, viscous precipitate which clogged the separatory funnel. The water wash formed a suspension which failed to break up upon addition of sodium chloride. As a consequence of these developments, it was possible that the free benzene from each wash did not contain all the product formed.

Result The free benzene from the washes, which was black in color, was filtered three times through activated charcoal and filter cel in an attempt to decolorize it. A partial decolorization was obtained. The decolorized solution was evaporated on a hot plate, yielding 0.5 gm. of dirty yellow crystals. The suspension mentioned above developed a benzene layer again upon setting overnight. The black precipitate was re-extracted with benzene. The extracts were combined, filtered through



activated charcoal, and evaporated to dryness. The yellow crystals obtained (0.05 gm.) were combined with the others.

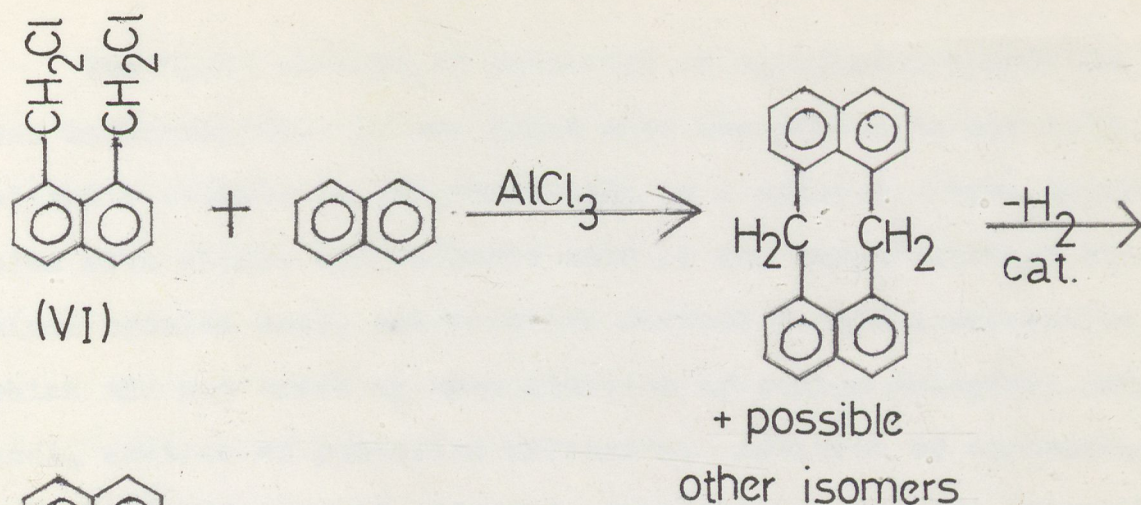
The combined yellow crystals were chromatographed on an alumina column of activity I. They were introduced to the column in a 50-50 benzene-petroleum ether mixture. Petroleum ether was used as eluant. Various fractions were collected and evaporated. All were white and crystalline in form. Some crystal fractions melted as low as 78°, while the highest melting fraction melted at 98° to 102°. Letsinger found 1,8-dibromonaphthalene to melt at 95° to 100° after one recrystallization and at 106° to 108° after three recrystallizations (9).

Upon collecting all those crystals with melting points 95 or higher, 0.2 gm. was obtained. This was a 0.6% yield, based on all of the 1,8-diaminonaphthalene reacting. An infrared spectrum of the product supported the conclusion that 1,8-dibromonaphthalene was obtained since characteristic amine absorption bands were missing, and the spectrum matched the  $\lambda^{KBr}$  reported by Letsinger in the above reference.

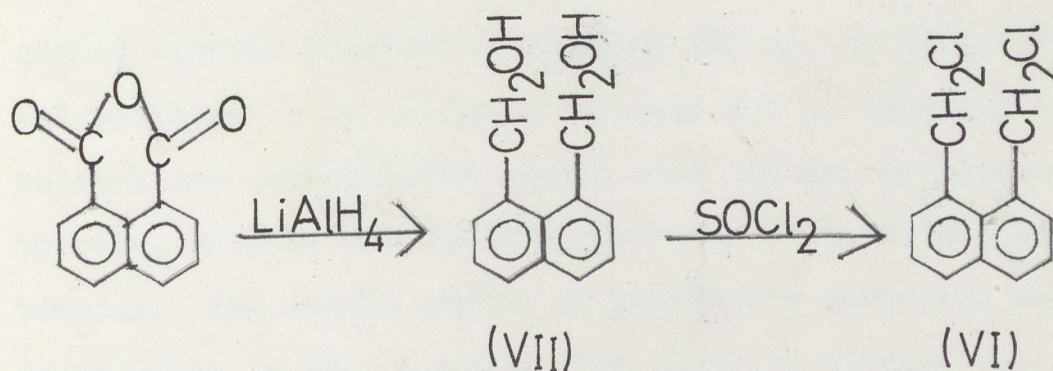
#### Reaction 2.

Having failed to obtain 1,8-dibromonaphthalene in great enough quantity for further synthetic work, it was decided to try a different approach to the synthesis of (II). An alternate procedure involving the Friedel-Crafts addition of 1,8-di(chloromethyl)naphthalene (VI) to naphthalene, followed by dehydrogenation to yield (II) was devised. This synthesis is shown on the next page.





Compound (VI) was to be obtained from the chlorination of 1,8-dimetholnaphthalene (VII), which is produced by the reduction of naphthalic anhydride. This was Reaction 2 (the reduction only). It is shown below.





The first attempt at reduction of naphthalic anhydride was unsuccessful. It was found that the anhydride was only slightly soluble in the ether used as a solvent. Upon destruction with dilute hydrochloric acid of the excess lithium aluminum hydride used, the reaction mixture formed a suspension which did not break up upon addition of sodium chloride, methanol, acetone or potassium hydroxide. Addition of concentrated hydrochloric acid effected a separation, but the ethereal extract was found to be a highly viscous substance (probably polymeric) upon separation. Separation was finally obtained by gravity filtration of the reaction mixture through sodium chloride previously wet with ether. An infrared analysis revealed that reduction was not complete. This will be discussed more thoroughly in the discussion section below.

A more efficient apparatus was then employed for the reduction. It overcame the problem of the low solubility of naphthalic anhydride in ether. The method was taken from Beyler and Sarett (10). A mechanically stirred suspension of 3.8 gm. of lithium aluminum hydride in 400 ml. of tetrahydrofuran was refluxed in an apparatus (Figure 2.) so arranged that hot solvent was continuously washed over 8.6 gm. of naphthalic anhydride, rinsing dissolved portions of it into the hydride suspension. The entire amount of naphthalic anhydride was dissolved in 24 hours in this manner. The reaction mixture was allowed to cool overnight. Excess lithium aluminum hydride was then decomposed by dropwise addition of 10% hydrochloric acid.

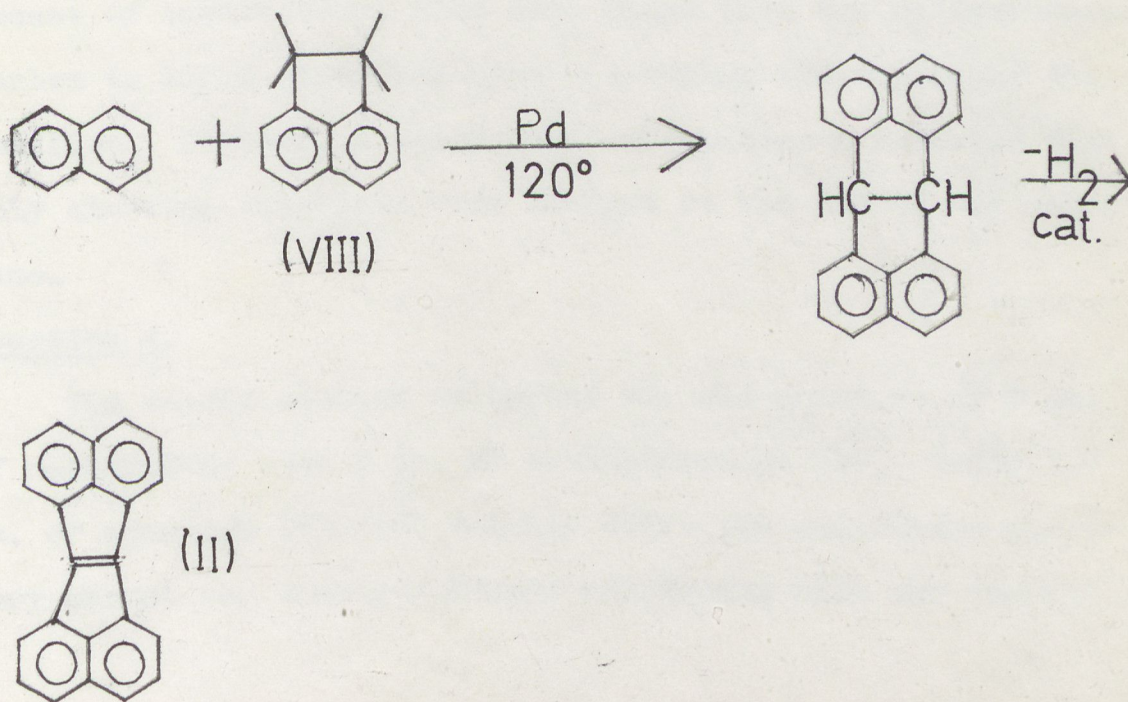


The reaction mixture, an olive drab suspension, was then filtered through anhydrous sodium sulfate. Additional fresh tetrahydrofuran was washed through the material in the filter paper to further aid in extraction. Upon evaporation of most of the solvent, the first recrystallization yielded 1.23 gm. of large light brown rectangular crystals having a melting point of 160°-161°, compared with Beyler and Sarett's value of 158° (11). The yield for the reaction was 15%.

### Reaction 3.

Having obtained (VII), it was decided to suspend this synthetic route in favor of attempts at shorter, more direct Friedel-Crafts and somewhat related closures to make (II).

The first of these closures attempted was the reaction of acenaphthene (VIII) and naphthalene in the presence of the dehydrogenating agent palladium-on-carbon. The reaction is shown below.





Forty gm. of naphthalene, 5 gm. of (VIII), and approximately 10 gm. of 5% palladium-on-carbon were placed in a three-necked flask. One neck of the flask was used as an inlet for nitrogen gas and another as an exit for the gas. This precaution was taken in case hydrogen gas should be liberated fast enough from the reaction to present a danger of explosion. The third neck of the flask contained a thermometer. The flask was placed in a heating mantle. Both mantle and flask were covered with aluminum foil to retain the heat. The temperature of the reaction mixture was maintained at about 120°. At this temperature, the reactants were in a liquid state, since naphthalene melts at 80° (12) and acenaphthene at 95° (13). The nitrogen exit neck was fitted with a mechanical stirrer, which nevertheless allowed the nitrogen gas to escape. The mixture was stirred at 120° overnight.

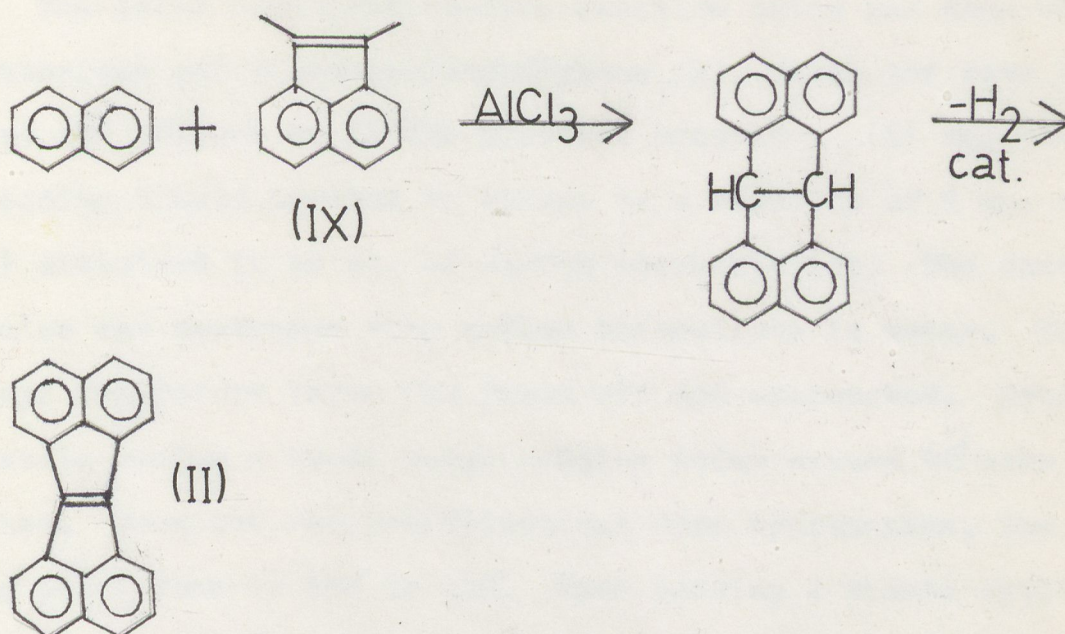
A color change from essentially white, due to the large amount of naphthalene, with some black from the palladium-on-carbon to light green was observed during the course of the reaction. However, a vapor phase chromatogram revealed that only starting materials were present at the end of the reaction time.

#### Reaction 4.

The second closure attempted was the reaction of 9 gm. of naphthalene with 1 gm. of acenaphthylene (IX), using 1.7 gm. of aluminum chloride (almost twice the calculated necessary amount for complete  $\pi$ -type complexing with the olefin)



as a catalyst.



Cyclohexane, in the quantity of 150 ml. was employed as a solvent. It was first tested with permanganate reagent to insure that there were no double bonds present in it which could react in place of (IX).

The reaction was carried out at room temperature with constant mechanical stirring for three hours. A color change from initial yellow to medium dark green was observed during this time. The excess aluminum chloride was destroyed with a small volume of dilute hydrochloric acid. Inorganic salts and water present were removed by filtering the solution through sodium chloride. A vapor phase chromatogram showed that only starting materials were present.

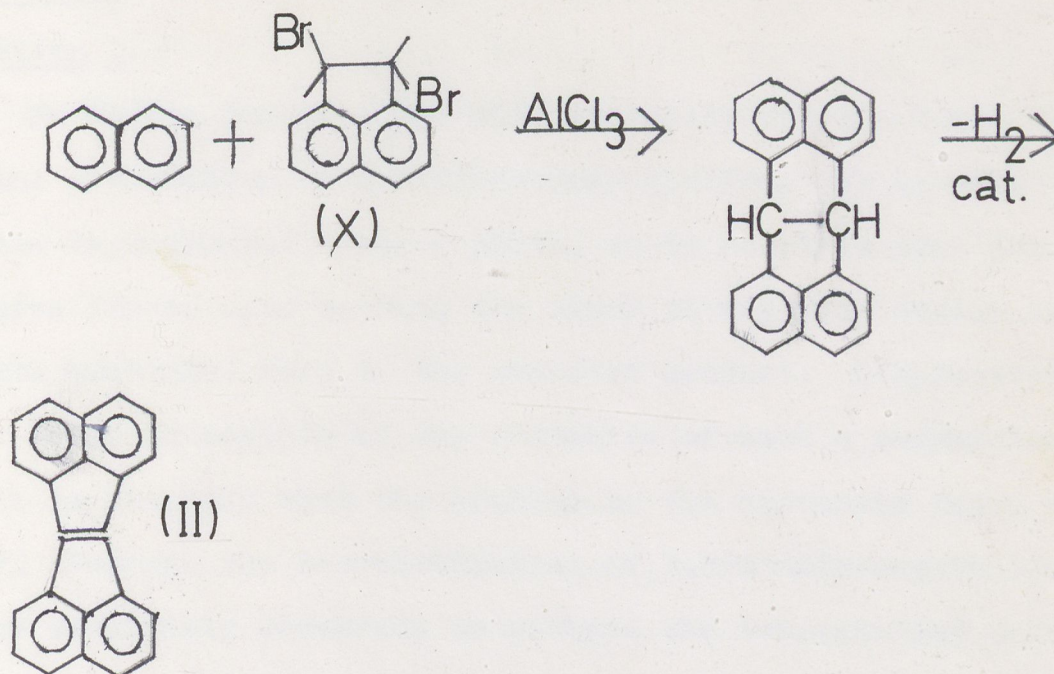


Reaction 5.

The third condensation-type reaction tried was done with naphthalene and dibromoacenaphthylene (X), using the same catalyst and solvent as in the previous reaction. (X) was obtained by adding liquid bromine in excess to a solution of 2 gm. of (IX) dissolved in 40 ml. of carbon tetrachloride. The excess bromine was destroyed with sodium thiosulfate in water. The orange chloroform layer was drawn off and evaporated. Orange crystals having a broad range melting point around 98° were obtained. Upon two recrystallizations from cyclohexane, the melting point rose to 106° to 108°. Upon passing a dilute cyclohexane solution of the twice recrystallized substance through an alumina column of activity I, 0.6 gm. of yellowish-orange crystals having a melting point of 116° to 118° were obtained, compared with the literature value of 121° to 123° (14). The reaction went in 15% yield.

Approximately 0.54 gm. of (X) was mixed with 9 gm. of naphthalene and 2.2 gm. of aluminum chloride in 75 ml. of cyclohexane. The reaction was stirred mechanically for three hours, by which time the originally orange-colored solution had turned greenish-black in color. The reaction is shown on the next page.





The large excess of aluminum chloride was then destroyed with a small amount of dilute hydrochloric acid. The reaction mixture was filtered through sodium chloride to remove the aluminum salts and the small amount of water from it. The solution was now seen to be dark orange in color. Vapor phase chromatography results were non-definitive and are treated in the discussion section below.



## Discussion

### Reaction 1.

No reason can be cited with certainty for the low yield in the preparation of 1,8-dibromonaphthalene, but as mentioned in the experimental section above, it is possible that the suspension formed upon washing the black slurry with sodium carbonate contained most of the expected product. Klopfenstein (15) makes no mention of the formation of such a suspension, so it is possible that the problem in the synthesis began earlier. Perhaps the tetrazotization of 1,8-diaminonaphthalene never completely occurred, or perhaps the tetrazotized material did not react completely.

This last assumption is supported by the fact that blue crystals were recovered from the black cake. They suggest that much of the cuprous bromide failed to react as part of the desired Sandmeyer reaction. This suggests that not very much tetrazotized material was available for reaction. Although the crystals did not fit the classic description of cuprous bromide, they probably contained copper since it was the only metal available which would form compounds of a high melting point. The blue crystals failed to melt by 285°. The copper was probably complexed in some way, since a flame test of the blue crystals showed a green flame with much black residue.

Letsinger also experienced low yields of 1,8-dibromonaphthalene using the tetrazotization method. He characterized them as too low to be of synthetic value (16). The method em-



ployed by Letsinger, as cited in the above source, was a Hunsdiecker conversion of 8-bromo-1-naphthoic acid from naphthalic anhydride, through the intermediate 8-hydroxymercuri-1-naphthoic acid as described by Rule et. al. (17). It was decided for this project that this synthetic route was too long to attempt.

### Reaction 2.

The Friedel-Crafts and related synthetic approaches to (II) appear to have been attempted in contradiction to Agosta's finding that he was unable to close (IV) by Friedel-Crafts methods. His efforts were described in the introduction. However, one would expect the compounds proposed or actually used in this project, namely (V), (VI), (IX), and (X), to react better under Friedel-Crafts conditions than (IV), or its acid chloride. This is predicted on the basis of a more stable carbonium ion intermediate being formed from the former series of compounds than from (IV). All the compounds, (IV) included, are expected to experience aryl resonance-stabilized carbonium ion intermediates, but compound (IV) should have a destabilizing factor of a highly electronegative oxygen atom attached to the carbonium carbon. Since Agosta was attempting to synthesize (III), he must have left both oxygen atoms intact throughout his attempts to close (IV).

Turning now to Reaction 2 specifically, the infrared spectrum of the sodium chloride-filtered aliquot of the first attempted lithium aluminum hydride reduction of naphthalic anhydride



showed much carbonyl absorption around 6.0 microns. The aliquot which had been extracted using concentrated hydrochloric acid, and which was viscous in nature, gave an infrared spectrum that was crowded with many sharp peaks, suggesting not the presence of more than one material, but possibly a polymer. These spectra were run by evaporation of an ether solution on a salt plate.

The success of the second attempt of the reduction of naphthalic anhydride was proved by an infrared comparison of the product with naphthalic anhydride. It was seen that the carbonyl areas were missing, as expected, from the product's spectrum. In addition, the product showed hydroxyl absorption around 3.0 microns. Moreover, the melting point agreed within 2° of the previously cited literature value.

### Reaction 3.

Reaction 3 was run with an excess of naphthalene in the hope that condensation of (VIII) with naphthalene would be more favorable than that of (VIII) with itself. The expected orientation is at the more reactive  $\alpha$ -positions of naphthalene. The ring shown in the reaction scheme in the experimental section might be closed (as is shown there) immediately by the palladium-on-carbon, or it could be closed and dehydrogenated to (II) by a stronger dehydrogenating agent later. The bond distance is favorable for this closure to an 8-membered ring.

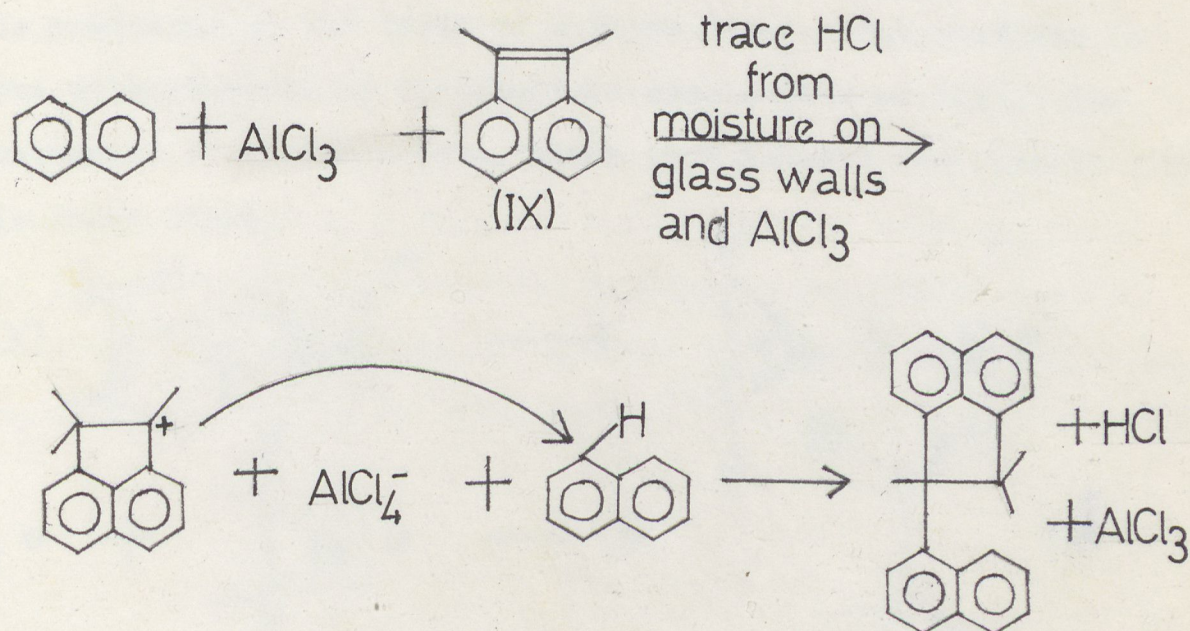
The vapor phase chromatography (VPC) for this reaction and for Reactions 4 and 5, was done from 220° to 230° using the



Perkin-Elmer O-column with cyclohexane as a solvent. This temperature was well below the melting point of (II), which is  $284^{\circ}$  to  $285^{\circ}$  (18). The VPC analysis of Reaction 3 showed naphthalene and acenaphthene in the 8 to 1 ratio in which they were introduced as reactants, with the naphthalene coming off the column first. Perhaps the only variable which might be changed to make this reaction work is a stronger dehydrogenating agent such as selenium dioxide.

#### Reaction 4.

Reaction 4 was run with a large excess of naphthalene in order to provide statistically that any carbonium ion formed from (IX) would react with naphthalene and not with another molecule of (IX). Again, perhaps the expected reaction product shown above in the experimental section is misleading. Perhaps a more likely reaction would form only one bond between (IX) and naphthalene. A proposed mechanism for the reaction is given below.

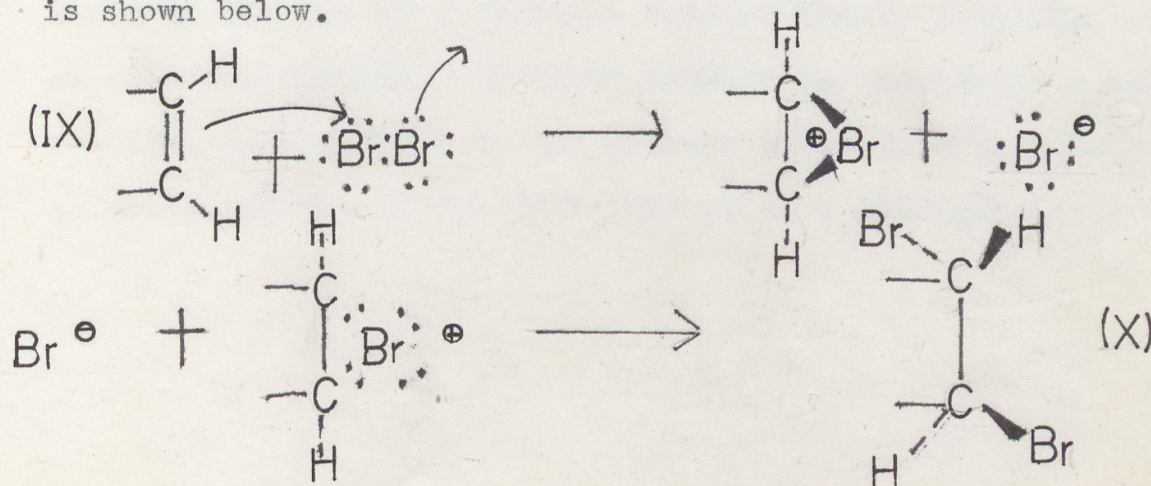




However, the VPC showed only naphthalene and (IX) in a 9 to 1 ratio, with the former coming off the column first. It was thought originally that an adduct had been formed, since the VPC peak corresponding to (IX) had a large trailing shoulder on it. (IX) itself was irregular in appearance upon being received from the Aldrich Chemical Company. There were both wet-looking yellow crystals and brown lumps present. When (IX) was run on the VPC in cyclohexane by itself, the same peak with the shoulder was observed. The shoulder was approximately  $\frac{1}{4}$  the height of the main peak, showing, therefore, a large amount of impurity.

#### Reaction 5.

The dibromination of (IX) is postulated to have occurred in such low yield due at least in part to the impurity of (IX). Again, the reaction of (X) with naphthalene would probably form only one bond between (X) and naphthalene due to the expected trans-orientation of the bromine atoms. The trans-orientation is predicted on the basis of a bromonium-ion intermediate in the dibromination of the olefinic double bond of (IX). The mechanism of dibromination, taken from Roberts and Caserio (19), is shown below.





As stated before, the VPC for this reaction was not definitive. Peaks for naphthalene and (X) were identified and verified by running each of these reactants alone on the same column in the same solvent at the same temperature. The times at which they came off correlate perfectly with two of the peaks on the chromatogram of Reaction 5. However, a small additional peak was observed in duplicate runs of the Reaction 5 chromatogram. Its position indicates that it came off the column before the naphthalene did. It represents approximately one two-hundredth as much material as naphthalene. Since naphthalene, (VIII), (IX), and (X) all came off the column in ascending order of molecular weight, it is highly unlikely that this peak is an addition product. At this time its origin remains unknown, since a sample of the naphthalene used in the reaction failed to give such an early peak. If time had permitted it, the isolation from the VPC of an amount of substance from this early peak great enough for an ultraviolet spectrum would have been attempted.

Reactions 4 and 5 represent an increase in strength of Friedel-Crafts conditions employed. The next logical step would be the use of a stronger Friedel-Crafts catalyst, such as aluminum bromide. Aluminum bromide is considered a more reactive catalyst due to its greater solubility in hydrocarbon solvents and due to the fact that it is a stronger Lewis acid (20).

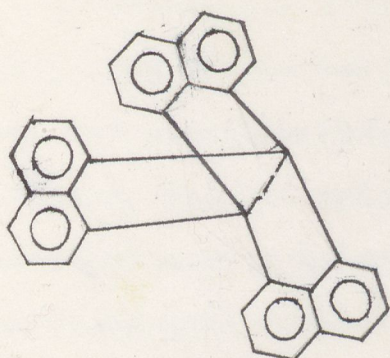


### Conclusion

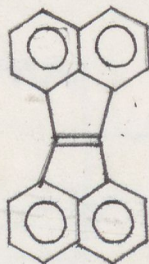
In view of the difficulty of achieving simple Friedel-Crafts additions to prepare (II), perhaps the quickest experimental course would be to use Letsinger's method of dibromination and to then follow his synthesis. As mentioned in the introduction above, (II) could be dibrominated to (V) and reacted in a Friedel-Crafts manner to obtain (I). However, since the synthesis of (I) as approached in this project ultimately depends upon this last Friedel-Crafts addition, increasingly strenuous conditions should be imposed upon Reactions 4 and 5 and related additions until two bonds between naphthalene and the other reactant are achieved. If this proves to be impossible, it is highly doubtful that (V) could be reacted with naphthalene under Friedel-Crafts conditions to yield (I).



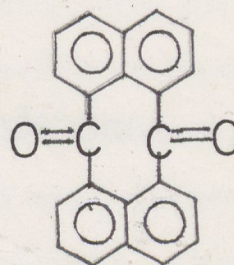
Figure 1. Compounds in the Synthesis



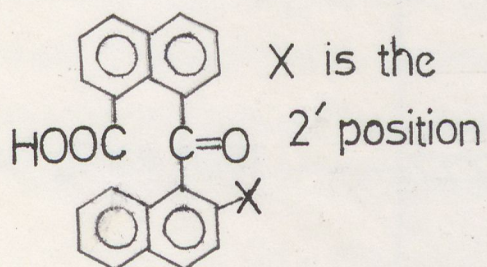
(I)



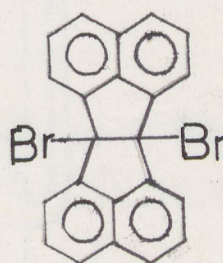
(II)



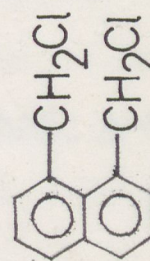
(III)



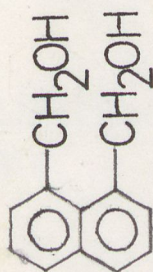
(IV)



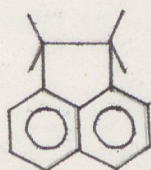
(V)



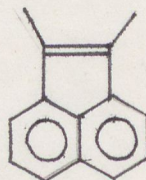
(VI)



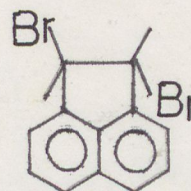
(VII)



(VIII)



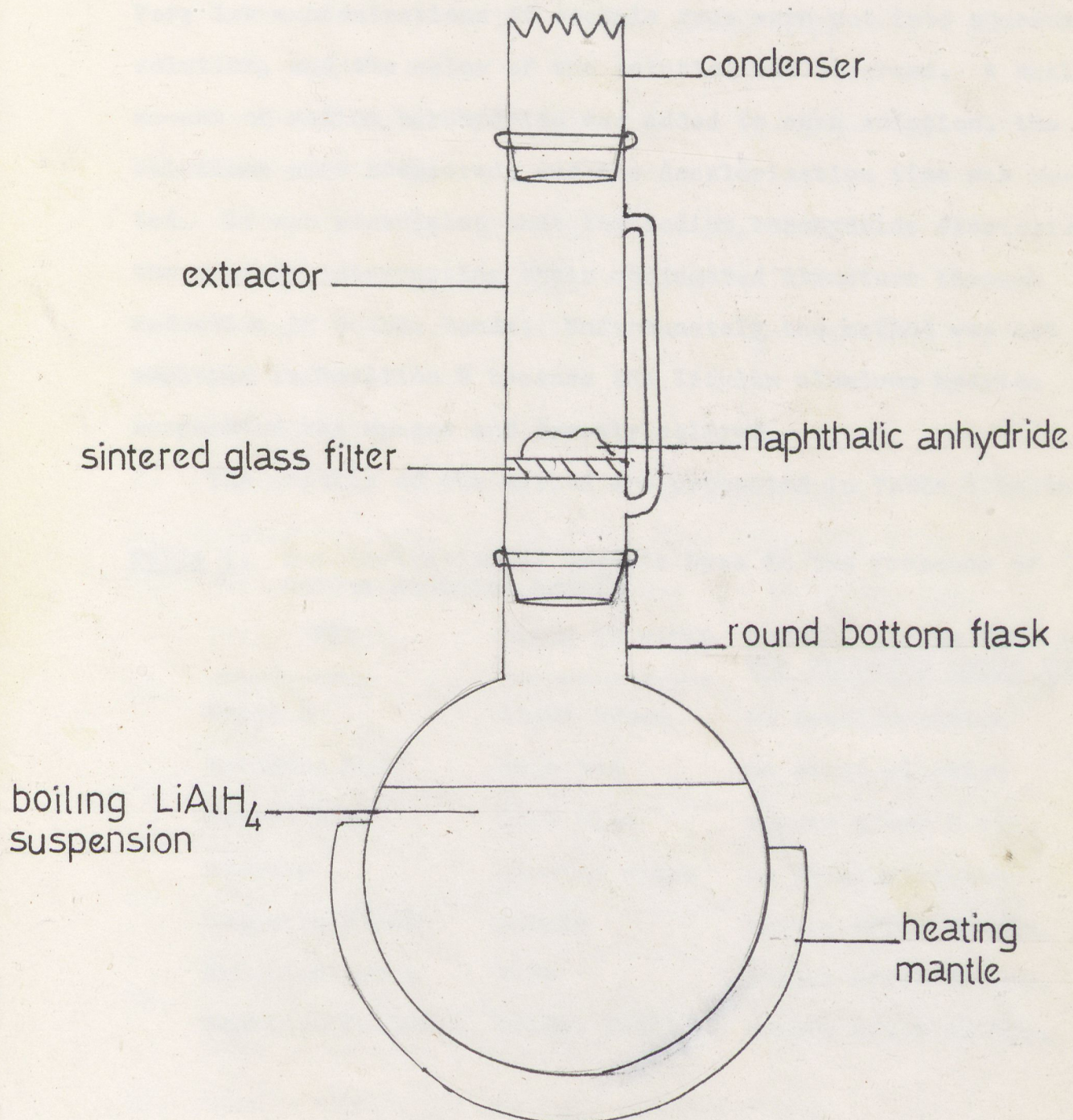
(IX)



(X)



Figure 2. Modified Soxhlet Extractor for Reaction 2





## Appendix

A method for determining the presence of active reducing agent in solution was devised in conjunction with this project. Very low concentrations of organic dyes were put into aqueous solution, and the color of the solution was observed. A small amount of sodium borohydride was added to each solution, the solutions were stoppered, and the decolorization time was noted. It was postulated that the sodium borohydride decolorized the dyes by interrupting their conjugated structure through reduction of double bonds. Unfortunately, the method was not employed in Reaction 2 because the lithium aluminum hydride suspension was opaque and densely colored.

The results of the method are presented in Table 1 below.

Table 1. Decolorization of Organic Dyes in the Presence of Active Reducing Agent

<u>DYE</u>	<u>COLOR IN WATER</u>	<u>DECOLORIZATION TIME AFTER REDUCING AGENT ADDED</u>
Ursol D	light brown	no decolorization
Acridine Red	dark red	no decolorization
Patent Blue	dark blue	occurs after 5 min.
Uranine	glowing green	no decolorization
Columbia Black	purple	occurs after 30 min.
Erioglancine A	blue	occurs after 10 min.
Naphthol Yellow L	bright yellow	occurs after 30 min.



Bibliography

1. Roberts, J.D., and Caserio, M.: Basic Principles of Organic Chemistry, W.A. Benjamin, Inc., New York, 1965, p.227.
2. Gerson, F., and Martin, W.B.: J. Am. Chem. Soc., 91, 1883-1891, (1969).
3. Letsinger, R.L., and Gilpin, J.A.: J. Org. Chem., 29, 243-244, (1964).
4. Agosta, W.C.; J. Am. Chem Soc., 89, 3505-3510, (1967).
5. Knapp, W.: Monatsh. Chem., 67, 332, (1936).
6. Letsinger, R.L., and Gilpin, J.A.: J. Org. Chem., 29, 244, (1964).
7. Klopfenstein, C.: private communication.
8. Hodgson, H., and Walker, J.: J. Chem. Soc., 1620, (1933).
9. Letsinger, R.L., et. al.: J. Org. Chem., 27, 672, (1962).
10. Beyler, R.E., and Sarett, L.H.: J. Am. Chem. Soc., 74, 1411, (1952).
11. Beyler, R.E., and Sarett, L.H.: J. Am. Chem. Soc., 74, 1411, (1952).
12. Handbook of Chemistry and Physics, 44<sup>th</sup> ed., The Chemical Rubber Publishing Co., Cleveland, 1961, p.1107.
13. Handbook of Chemistry and Physics, 44<sup>th</sup> ed., The Chemical Rubber Publishing Co., Coeveland, 1961, p.767.
14. Dictionary of Organic Compounds, 4<sup>th</sup> ed., Oxford University Press, New York, 1965, p.6.
15. Klopfenstein, C.: private communication.



16. Letsinger, et. al.: J. Org. Chem., 27, 672, (1962).
17. Rule, H.G., et. al.: J. Chem. Soc., 168-171, (1934).
18. Letsinger, R.L., and Gilpin, J.A.: J. Org. Chem., 29, 244, (1964).
19. Roberts, J.D., and Caserio, M.: Basic Principles of Organic Chemistry, W.A. Benjamin, Inc., New York, 1965, p.179.
20. Olah, G.A.: Friedel-Crafts and Related Reactions, Interscience Publishers, New York, 1963, v.1., p.249.