Synthesis
SYNTHESIS OF ANTHRACENE

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## Thesis: Synthesis of Anthracene

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I: Introduction

Naphthalene, one of the chief solid hydrocarbons of coal tar is usually graphically represented as containing two aromatic nuclei \[ \text{\includegraphics[width=0.1\textwidth]{naphthalene.png}} \]; likewise anthracene, another solid hydrocarbon occurring in coal tar in very small amounts, is represented as made up of three aromatic nuclei \[ \text{\includegraphics[width=0.15\textwidth]{anthracene.png}} \]. So far as is known, however, a synthesis of the latter, in which the naphthalene nucleus was maintained intact has never been carried out. The object of the researches reported in this thesis was to prepare a derivative of naphthalene, in which its nucleus would not be destroyed, from which anthracene could be obtained.
II: Historical: Theoretical

Anthracene itself was first obtained by Dumas and Laurent\(^1\) in 1832 from the high boiling fraction of coal tar. From a determination of the vapor density of the new compound Dumas gave it the formula \(C_{70}H_{12}\) and later investigations by Laurent\(^2\) appeared to confirm the results. Since the new substance was supposed to be a polymer of naphthalene Dumas gave it the name "paranaphthalene" but Laurent in his later publications definitely assigned to it the name "anthracene".

The first accurate characterization of anthracene seems to be due to Fritzsche\(^3\) who identified the hydrocarbon \(C_{14}H_{10}\) but he apparently did not know that it was the same substance previously described by Dumas and Laurent. During the next thirty-five years the interest in anthracene was of a somewhat disconnected nature altho new facts regarding its chemical and physical properties were contributed by Fritzsche\(^4\), Anderson\(^5\), Laurent\(^6\), Barbier\(^7\) and others.

In 1870 - a preliminary note\(^8\) was published in 1868 - Graebe and Liebermann\(^9\) published their classical article in which they correlated the knowledge of anthracene that was available at that time and showed particularly that alizarin, the coloring matter obtained from the madder root, could be reduced by distillation with zinc dust and hydrogen to anthracene. The investigations of these men, together with those of Perkin\(^10\) in England, gave a marked impetus to researches with anthracene and until the close of the nineteenth century it furnished a basis for one of the most fruit-
ful series of investigations of that time.

The synthesis of anthracene during this half century formed by no means a small portion of the investigations. The different synthetical methods have, however, been so admirably grouped and summarized by Jackson and White that only a few of those which have some particular bearing upon the structure of anthracene will be mentioned.

Limpricht\textsuperscript{12}, a couple of years before the publication of Graebe and Liebermann showed that he could obtain anthracene by heating benzyl chloride with water in a sealed tube for eight hours at 190°. From this synthesis it might be inferred that anthracene had the structure C\textsubscript{6}H\textsubscript{5}-C≡C-C\textsubscript{6}H\textsubscript{5} but Schölemmer\textsuperscript{13} in 1872 pointed out that since alizarin could be oxidized to phthalic acid such a structure must be rejected. He considered it probable that anthracene was built up from three aromatic nuclei and therefore had the structure \[ \begin{array}{c} \text{C} \text{C} \\ \text{C} \text{C} \end{array} \] In fact this structure was at one time favored by Graebe and Liebermann on the strength of Limpricht's synthesis.

A few years later (1872) Behr and Dorp\textsuperscript{14} showed that anthracene could be formed by passing o-benzyl toluene over heated lead oxide; and Dorp\textsuperscript{15} the next year showed that the same result was obtained when the o-benzyl toluene was simply passed thru a hot tube. This type of synthesis pointed to the structure \[ \begin{array}{c} \text{C} \text{C} \\ \text{C} \text{C} \end{array} \] rather than to the one suggested by Schölemmer. Some of the other syntheses of anthracene during this period are those reported by Perkin and Hodgkinson\textsuperscript{16} by treating benzyl chloride with aluminium chloride; Herzold by
action of phosphorus pentoxide on benzyl ethyl ether; Shramm from benzyl chloride and aluminium chloride in the presence of benzene; Jackson and White at Harvard by heating o-bromobenzyl bromide with sodium; Friedel and Crafts by treating benzene and methylene chloride with aluminium chloride; Anschütz by action of aluminium chloride upon tetrabromoethane in benzene; and Gresly by distilling o-benzyl benzoic acid with zinc dust.

A unique series of investigations of this period were those dealing with the polymerization of acetylene and the synthesis of such hydrocarbons as styrene, naphthalene, and anthracene by Berthelot. These investigations are particularly suggestive in the light of some recent observations upon the carbonization of coal and are of general interest in our problem of the synthesis of anthracene.

Berthelot carried out his investigations by passing a mixture of such hydrocarbons as acetylene, ethylene, and benzene thru a red hot tube at the rate of about one gram per minute, condensing, if possible, the products formed and then subjecting them to analysis. In this way he was able to identify a large number of products and formulate a theory of their formation and structure; only the naphthalene and anthracene need to be considered here.

Naphthalene is formed "in large amounts when a mixture of benzene and acetylene are passed thru a red hot tube". The reaction is explained by supposing that styrene is first formed, followed by a second reaction of the styrene on the acetylene.

\[
\begin{align*}
C_6H_6 + C_2H_2 &= C_8H_8 \\
C_8H_8 + C_2H_2 &= Cl_0H_8 + H_2
\end{align*}
\]
The last reaction is represented graphically:

\[
\text{Styrene} \quad \text{Naphthalene} \\
C_6H_4 \left[ C_2H_2(\text{H}_2) \right] + C_2H_2 = C_6H_4 \left[ C_2H_2(C_2H_2) \right] + H_2
\]

and Berthelot believed that the formula given for naphthalene is in harmony with its properties.

Likewise the anthracene which is formed in small amounts by passing acetylene thru a red hot tube is probably due to (a) the polymerization of acetylene to give benzene; (b) the condensation of benzene and another mole of acetylene to give styrene; and (c) the condensation of the styrene with benzene to give anthracene.

\[
\begin{align*}
3C_2H_2 & = C_6H_6 \\
C_6H_6 + C_2H_2 & = C_8H_8 \\
C_8H_8 + C_6H_6 & = C_{14}H_{10} + 2H_2
\end{align*}
\]

The formula representation of anthracene to show its relationship to naphthalene and benzene is given as \(C_8H_4 \left[ C_6H_4(C_2H_2) \right]\). This formula suggests that anthracene contains two benzene nuclei and a \(C_2H_2\) group which bears a relationship to the rest of the molecule that is different from other carbon and hydrogen atoms. Indeed the formation of such hydrocarbons as styrene, naphthalene, and anthracene may be considered as the addition of one, two, or three equivalents of acetylene (or ethylene) to one or two equivalents of benzene with or without the elimination of hydrogen. Berthelot points out particularly that styrene, naphthalene, and anthracene are not formed by a similar heating of pure benzene.

Naphthalene can be shown to consist of two aromatic nuclei, and since anthracene resembles it in so many ways it is usually given the three aromatic nuclei structure of which
are the most general.

Some of the syntheses of anthracene point to the first structure - bridge structure -, others to the second, and from still other syntheses it may be considered to have either the first or second structure. The reaction of aluminium chloride with tetrabromoethane in the presence of benzene to give anthracene seems to suggest structure (a).

The structure of anthracene from its formation by heating o-benzyl toluene in a red hot tube or by passing its vapors over hot lead oxide in which there is a loss of hydrogen as

and the elimination of all the bromine atoms and two hydrogen atoms from two moles of o-bromobenzyl bromide by heating it with sodium as

may receive as satisfactory explanation by one formula as by the other, with the evidence perhaps somewhat favoring the bridge structure.

Beilstein, using the work of Peckmann, Liebermann and Perkin as a basis, gives a series of reactions which indicate the structure of anthracene about as well as any that have been suggested. If bromo-o-phthalic acid is condensed with benzene
by means of aluminium chloride, bromobenzoyl benzoic acid is formed. In the bromo-o-phthalic acid we know that the carbonyl groups are attached to adjacent carbon atoms in the benzene nucleus. If the bromobenzoyl benzoic acid is heated with sulfuric acid to 180° or treated with phosphorus pentachloride it is converted into bromoanthraquinone. The bromoanthraquinone when heated with potassium hydroxide to 160° gives hydroxyanthraquinone and this by oxidation with nitric acid gives phthalic acid. Since the benzene nucleus which comes from the bromo-o-phthalic acid is the one destroyed then it follows that the two carbonyl groups are combined with adjacent carbon atoms in anthraquinone. Since hydroxyanthraquinone, upon reduction with zinc dust and hydrogen, yields anthracene the structure of the latter is also shown.

Acridine, a compound somewhat related in structure to anthracene is formed by heating formyl diphenyl amine with zinc chloride.
From the method of its formation acridine then may appear to contain a bridge bond in the central nucleus and from analogy the same structure may be suggested for anthracene.

Anthracene is easily oxidized by chromic acid in glacial acetic acid to anthraquinone but it has been suggested by Lagodzinski\(^{29}\) that the reason the central nucleus is attacked rather than one of the other is the fact that the two carbon atoms joining the two outside nuclei are symmetrically situated with respect to the whole molecule rather than to a peculiar bridge structure. He has shown that 1-amino-2-hydroxyanthracene upon treatment with chromic acid and sulfuric acid is oxidized to 1-2-anthraquinone; a reaction which would ordinarily easily oxidize the 9-10 positions in the central nucleus. Apparently the presence of the amino and the hydroxyl groups in the 1-2 positions so stabilizes the central nucleus that it is not easily attacked.

In this connection it may be noted that Bamberger\(^{30}\) considered that since the ether of anthrol can be formed by heating it with hydrochloric acid and alcohol to 150° and cannot be similarly formed with 2-hydroxyanthraquinone, there must be a difference in their structure which he represented as

That is in 2-hydroxyanthraquinone there are two complete benzene nuclei and an ether is no more easily formed with it than with phenol.
Armstrong gives the same structure for anthraquinone but contends that anthracene itself does not have a symmetrical structure. He represents anthracene as follows

Hewitt to explain the fluorescence of anthracene suggests that there is probably an equilibrium between

We may return to our first statement and say that there is evidence both for and against either of the two general structures

It will be noticed that none of the syntheses which have been mentioned - the work of Berthelot may possibly be excepted - have retained a naphthalene nucleus or have started with naphthalene, and, as has already been mentioned, so far as is known such a synthesis has never been made. If one could start with naphthalene and by a series of reactions obtain anthracene without destroying the naphthalene nucleus then we would have a much clearer idea of the structure of anthracene. In the research, of which this is a report, the actual naphthalene nucleus was not retained in the final step, but a derivative of naphthalene was prepared from which anthracene was obtained by distillation with zinc dust.
III: Experimental

Altho the first line of investigation which was attempted proved unsuccessful, it has seemed best to make a short report of the work since it includes a few items of interest and shows some of the peculiar properties of naphthalene and naphthalene derivatives. Only the first two steps of the following representation of a series of reactions which indicate how it was hoped to prepare anthracene and still retain a naphthalene structure in closing up the last nucleus was carried out.
1. Dihydronaphthalene

One of the peculiar properties of naphthalene and of naphthalene derivatives is that their reactions go more smoothly when they are handled in small quantities. This was found to be particularly true in the reduction of naphthalene and the bromination of the resulting dihydronaphthalene.

The procedure as outlined by Bamberger and Lodter\(^{33}\) of allowing a boiling solution of 15 grams of naphthalene dissolved in 300 grams of absolute alcohol to flow in a slow stream on to 22.5 grams of finely sliced sodium was found not to give as good yields of the dihydronaphthalene as when 10 grams of naphthalene dissolved in 150 cc of absolute alcohol was heated to boiling and poured rapidly upon 18 grams of sodium. A sketch of the apparatus is given in figure I. By this procedure a more vigorous reaction is brought about and the temperature of course does not exceed that of the boiling alcohol and little if any tetrahydronaphthalene is formed.

To separate the dihydronaphthalene from the sodium the alcohol and the unchanged naphthalene, a single reaction product or a composite of several sets of reductions was subjected to steam distillation. The distillation at first is carried out quite slowly. By careful work it is possible to remove most of the unchanged naphthalene along with the alcohol; some dihydronaphthalene will pass over, however. After the
alcohol has all been removed the rate of distillation is increased and the dihydronaphthalene rapidly distilled over. It settles to the bottom of the water solution as a rather heavy oil and may be removed by extraction with ether. Upon evaporation of the ether the dihydronaphthalene is obtained as a yellow oil which may be congealed to a solid that melts at about 8-10°; the perfectly pure dihydronaphthalene melts at 15.5°. The best yields that were obtained approximate 60% of the theory. The product is undoubtedly impure dihydronaphthalene since the unchanged naphthalene would be carried along to a greater or less extent by the above separation. It was found, however, to be sufficiently pure for the purpose of preparing the dibromotetrahydronaphthalene.

2. Dibromotetrahydronaphthalene

Dihydronephthalene acts like an unsaturated compound of the ethylene type and adds hypochlorous acid to give the tetrahydrochlorohydrin, and bromine to give the dibromotetrahydro-

aphthalene.

The dibromotetrahydronaphthalene was prepared in two ways: (a) by the method of Bamberger and Lodter and (b) by aspirating bromine vapors into a chloroform solution of the unsaturated compound.

The method of Bamberger and Lodter consists simply in adding drop by drop and with constant shaking the required amount of bromine dissolved in quite a large volume of chloroform into a chloroform solution of the dihydronaphthalene kept cold by a freezing mixture of salt and ice. Upon evaporation of the
chloroform a reddish colored oil remains from which long needle-like crystals separate out after standing over night. To separate them from the oil in which the crystals are imbedded they were pressed between filter paper; upon recrystallization from methyl alcohol they have a melting point of 73-74°.

This method gives fairly good yields, provided the bromination is attempted in only small -using not over 25 grams of the dihydronaphthalene- lots. If a 5 or 10 grams sample is used the yield of dibromotetrahydronaphthalene obtained is but very little if any more than would be obtained with the 2.5 grams sample.

The method which was found to be most successful since larger quantities could be brominated to give yields equally as good as are obtained in the former method, consisted essentially in aspirating bromine vapors into a chloroform solution of dihydronaphthalene surrounded by a freezing mixture. Figure II shows a sketch of the apparatus used. The required amount of bromine

![Diagram](https://via.placeholder.com/150)

*Fig II*

was weighed out in the flask a and connected with the flask b containing the chloroform solution of dihydronaphthalene. The water bath surrounding a was then warmed and a slow stream of air drawn thru the apparatus. If the operation is carried out by adding the bromine in the solvent the brown color of the bromine is at first rapidly destroyed but a little later the color dis-
appears much more slowly; if the bromine is aspirated in then the brown color does not appear until just at the very end. The aspiration method of bromination gave yields approximating 80% of the theory and 10 to 14 grams samples were as successfully brominated as a smaller sample.

The dibromotetrahydronaphthalene was recrystallized from ethyl alcohol, in which it is fairly soluble, giving long white needle crystals which have a sharp melting point of 71.5-72°. These crystals however tend to discolor a little when exposed to the air.

3. Condensation with Malonic Ester

Attempts were made to condense malonic ester with the dibromotetrahydronaphthalene in two ways: (a) the usual method with sodium and alcohol as the condensing agent and (b) with magnesium and alcohol as the condensing agent.

In the first case 4 grams of the dibromotetrahydronaphthalene were refluxed with two moles -4.57 grams- of ethyl malonic ester; two atoms -0.657 grms- of sodium; and 35 moles -23 grams- of absolute alcohol but so far as could be determined no condensation whatever took place, the dibromo compound being recovered almost quantitatively unchanged.

The procedure used in the second attempt to condense the malonic ester with the dibromotetrahydronaphthalene was the same as that used by Noyes and Kyrikides\textsuperscript{36} for condensing ethylene bromide with malonic ester.

3.35 grams of magnesium turnings were treated with 133.5
grams of mercury and heated, with frequent shaking, on the steam bath until amalgamation was complete. Care was taken to keep the amalgam in a small area on the bottom of the flask. 35 cc of absolute alcohol were then added and the heating continued under a protected -CaCl₂- reflux condenser for about three hours. The crust of magnesium alcoholate which formed was broken up by several shakings. After cooling somewhat, 35 grams of malonic ester -ethyl- were added and the mixture again refluxed on the steam bath for three hours more. The alcoholic solution of the magnesium malonate was cooled a little and 20 grams of the solid dibromotetrahydronaphthalene were then carefully added and the refluxing on the steam bath continued for about eighteen hours. According to the above proportions twice the theoretical amount of magnesium malonate is used.

When the solution, resulting from the condensation of the dibromotetrahydronaphthalene with the malonic ester was allowed to stand about forty-eight hours crystals separated out. It was thought at first that possibly the desired condensation product was a solid. Attempts, however, to separate a solid ester failed; when filtration was tried the pores of the filter became quickly and completely filled and it was impossible to wash then clear with alcohol. When a portion was extracted with distilled water, acidified with nitric acid and silver nitrate added a precipitate of silver bromide was obtained. This indicated that (a) a condensation had taken place or (b) hydrobromic acid had split off and reacted with some magnesium to give magnesium bromide.

The whole of the product of condensation was transferred to
a Claisen distilling bulb and the alcohol and every thing which it was possible to separate up to a temperature of 100° using a pressure of 20mm to 25 mm was distilled over. Practically nothing came over after a temperature of 70° was reached.

The residue was then separated from the mercury by filtering thru an asbestos pad, acidified with hydrochloric acid, and thoroly extracted with ether. The ether extract was then returned to a modified Claisen bulb and the ether and every thing which would distill off up to a temperature of 100° -on water bath- and 20mm to 25 mm pressure, which was obtained by the use of the water pump, separated.

A Nelson oil vacuum pump was then substituted for the water pump and the distillation continued at the lowest pressure obtainable. The range between the point at which the first fraction and final fraction distilled was considerable; the first fraction distilled at 85-90° with a pressure of 5mm to 7mm, the second fraction 165-170° with a pressure of 15mm to 18 mm. Except for a very small amount of charring there was no indication of any decomposition. Nothing remained after the last fraction was separated.

The last fraction soon congealed to a solid mass. By recrystallization and taking its melting point it was found to be dibromotetrahydro naphthalene. In all a total of 15 grams of the original 20 grams of dibromo compound was recovered unchanged. It appeared that no marked condensation had taken place and the water soluble bromide, previously mentioned, must have come from the splitting off of hydrobromic acid. The method was abandoned for
The following one.

4. Representation of Series of Reactions Used in the Synthesis of Anthracene

The second series of reactions which were carried out resulted in a synthesis of anthracene. They were suggested by the work of Rabe who, starting with α-naphtoic acid, prepared phenanthrene. The graphical representation of the series of reactions which were used is as follows:

\[ \text{Anthracene} \xrightarrow{H_2SO_4, 160^\circ} \text{Phenanthrene} \xrightarrow{NaOH} \text{Phenanthrene} \xrightarrow{NaCN} \text{Phenanthrene} \xrightarrow{KOH} \text{Phenanthrene} \xrightarrow{NaOH, at 50^\circ} \text{Phenanthrene} \xrightarrow{\text{Alcohol, HCl}} \text{Phenanthrene} \xrightarrow{\text{CH}_3\text{C}^\circ\text{CH}_2\text{C}^\circ\text{C}_2\text{H}_5, \text{Na Alcohol}} \text{Phenanthrene} \xrightarrow{\text{HCl under pressure, Alcoholic KOH}} \text{Phenanthrene} \xrightarrow{\text{Zn Dust}} \text{Anthracene} \]
5. B-Naphthalene Sulfonic Acid

The naphthalene was sulfonated according to the method of Witt. 1000 grams of naphthalene were heated to 160° in an oil bath and 1600 grams of concentrated sulfuric acid added very gradually while the mixture was kept at 160° and in constant motion with an efficient stirrer. The clear somewhat darkened homogeneous solution was poured without cooling into 8000 cc of water. The warm solution was filtered thru an asbestos filter to remove a very small amount of sulfone and unchanged naphthalene. When the conditions were properly maintained practically 100% sulfonation was obtained. The filtered solution was evaporated to one-half its original volume and allowed to cool. The trihydrate of the b-naphthalene sulfonic acid crystallized out in beautiful silvery white slick scale-like crystals which were best separated from the mother liquor, which contains the more soluble a-isomer, by means of a centrifuge. Filtering on a cloth did not prove very successful since the crystals seem to stick together in such a way that the mother liquor is sucked off with great difficulty.

The b-naphthalene sulfonic acid was recrystallized by dissolving in 800 cc of hot water and 300 cc of concentrated hydrochloric acid, allowing the solution to cool and again centrifuging. The product obtained was silvery white in appearance and when dry had a "soapy" feeling due to the scale-like structure of the crystals. The yield was 70% of the theory.

The sodium salt was prepared by dissolving the b-sulfonic acid in hot water and adding a solution of sodium hydroxide.
sodium salt is much less soluble than the acid and extra hot water must be added to take all the salt into solution. The solution was allowed to cool down and the sodium salt filtered off; it is snow white and easily filtered off with suction but perhaps better handled in a centrifuge.

6. B-Naphtonitrile

Attempts to prepare the nitrile by distillation, under diminished pressure, of the sodium salt with potassium ferrocyanide as given by Derick and Kamm did not yield as good results as was expected. By this method it was possible to obtain yields of only 5-10% of the theory, whereas the above authors got 20% yields.

The method found best was to distill from an iron retort a mixture of equal parts of the sodium salt of b-naphthalene sulfonic acid and finely ground sodium cyanide; in many of the runs yields of b-naphtonitrile approximating 50% of the theory were obtained. For the distillation two types of retorts were devised and used, and, so far as could be determined, one was as efficient and satisfactory as the other; in both types a vacuum of 30 mm to 60 mm of mercury was maintained.

The first type of apparatus consisted of a one inch iron pipe eighteen inches long closed at both ends with an iron cap. The cap which could be taken off for charging the retort had a threaded hole in which a quarter-inch pipe, eight inches long, was screwed. To this outlet pipe a twenty-four inch condenser tube was attached leading to a side-neck distilling flask which in turn
was connected with the vacuum.

After the retort was charged with 60 grams of an equal mixture of the sodium salt and sodium cyanide it was arranged above a series of combustion-apparatus burners and the nitrile distilled out at as low a temperature as possible. The burners were lit one by one beginning at the end of the retort nearest the condenser. If the charge was heated too rapidly there was a tendency to froth and foam over and stop up the outlet. A sketch of the apparatus is given in figure III.

![Sketch of apparatus](image-url)

The second type of retort consisted of a one and one-half inch iron pipe, eight inches long, fitted with caps and a quarter-inch pipe outlet eight inches long. This outlet pipe, however, was bent so that the retort could be used in an inclined position as sketched in figure IV.

The apparatus was charged with 60 grams of an equal mixture of the sodium salt and sodium cyanide and the nitrile carefully distilled out by heating the charge beginning at the top.

In the use of both retorts the condenser was made to just dip into a small amount of water in the receiver so that the ni-
trile and other volatile material would not be carried over into and stop up the vacuum system. To hold the charge in place and to break up the froth a washer made by flattening out a wad of copper wire was used. The yields of crude nitrile were 25–50% of the theory.

7. B-Naphtoic Acid

The crude nitrile was not purified by redistillation but was transferred to a pyrex flask and hydrolyzed to the acid. The method of hydrolyzing, given by Baeyer and Besemfelder\(^40\), by refluxing with an equal mixture of concentrated sulfuric acid, glacial acetic acid, and water was used in a few cases but it always yielded an acid which was difficult to purify and left a residue which could be still further hydrolyzed with potassium hydroxide. Hydrolyzing with potassium hydroxide was found preferable since the reaction could easily be carried to completion, the danger of charring was entirely avoided, and a product was obtained which was easily purified without the use of bone black and repeated
recrystallizations. For carrying out the hydrolysis the nitrile was refluxed with 20-30% potassium hydroxide for about six to eight hours.

The hydrolysis of the crude nitrile by this method, however, left an unsaponifiable residue which is a reddish-colored liquid at the temperature of the hot water bath, but solidifies to a dirty red solid upon cooling. It is heavier than water; easily soluble in benzene but much more difficultly soluble in alcohol and ether. The identity of this substance and its other properties have not been further studied.

The solution resulting from the saponification of the nitrile was somewhat diluted and filtered while still hot thru a thick pad of asbestos. The filtrate was still further diluted and the b-naphtoic acid precipitated by adding concentrated hydrochloric acid. The precipitated acid was filtered off with suction, washed dissolved in dilute potassium hydroxide and again precipitated with hydrochloric acid. In this second precipitation it was found that if approximately normal hydrochloric acid was added until just a small precipitate was obtained, this precipitate would carry down practically all the coloring matter and impurities contained in the solution. By filtering this off and completing the precipitation with hydrochloric acid a product was obtained which would have only a slight yellow tinge and would melt within a degree of the correct melting point -185.5° of b-naphtoic acid.

The yields of b-naphtoic acid which were actually obtained approximated 20% of what could theoretically have been obtained from the sodium salt of the b-naphthalene sulfonic acid.
8. $\Delta^2$ -Dihydro b-Naphtoic Acid

The reduction of the b-naphtoic acid was carried out in ten gram portions according the method of Baeyer and Besemfelder by means of $\frac{3}{4}$ sodium amalgam. The b-naphtoic acid was dissolved in a small amount of dilute potassium hydroxide and diluted to 100-125cc. The solution was first cooled in an ice bath to a temperature of 4-5°, a slow steady stream of carbon dioxide was passed into it to neutralize the free alkali, and then 150 grams of crushed $\frac{3}{4}$ sodium amalgam added. The stream of carbon dioxide was continued and the mixture, with frequent shakings, allowed to stand in the ice bath until the reduction was complete. For determining the progress of the reduction small samples -0.5 cc- were withdrawn at regular intervals and tested with potassium permanganate as suggested by Derick and Kamm. These authors obtained complete reduction in forty minutes but in the several reductions which were made the time required was about an hour and a half. Reduction in the cold according to this procedure yields about 75% of the labile $\Delta^3$-dihydro naphtoic acid and 25% of the stable $\Delta^2$-dihydro naphtoic acid. In this work, however, only the stable form was desired so after separation of the mercury and carefully filtering thru an asbestos pad a small amount of sodium hydroxide was added and the solution heated on the water bath for an hour and a half. In this way a large part of the labile form was rearranged to the stable form.

After the solution had cooled the dihydro acids were precipitated with hydrochloric acid, filtered off with suction, washed,
again dissolved in potassium hydroxide, and finally reprecipitated in fractions, usually ten.

This method of separating the stable and labile isomers proved very successful. One reduction gave ten fractions whose melting-points without recrystallization were as follows:

Fraction 1 156-157°  Fraction 5 156-157°  Fraction 9 100°
  "  2 156-157°    "  6 157-158°    "  10 93°
  "  3 156-157°    "  7 152-155°
  "  4 156-157°    "  8 120-121°

These fractions were about equal in amount and therefore show that about 70% of the product was the stable Δ² isomer, 10% a mixture of the two forms, and 20% the labile Δ³ isomer. The correct melting-point for the stable is 161°; for the labile 101.2°. The yield of recrystallized Δ² dihydro b-naphtoic acid was about 65% of the theory.

9. Ethyl Ester of Δ² dihydro b-Naphtoic Acid

The Δ² dihydro b-naphtoic acid was esterified according to the method of Fischer and Speier. Ten grams of the acid were dissolved in 40 grams of absolute alcohol, 1 gram of dry hydrochloric acid gas added and the mixture refluxed for about six hours. On account of the tendency which sulfuric acid has to char it was not used.

About one-half of the alcohol was distilled off under reduced pressure -20 mm- and the remainder poured into four or five times its volume of water. Sodium carbonate was then added to neutralize the free hydrochloric acid that remained and to form the sodium salt of any unesterified dihydro acid. The ester was
then taken up in ether, the ether layer thoroughly washed with water in a separatory funnel, and the aqueous layer similarly washed twice with ether. The aqueous layer upon acidification gave only a small precipitate of dihydro acid showing that the esterification had been almost complete. The ether layer was transferred to a Claisen distilling flask and the ether removed on the water bath and the ester further dried at the temperature of the water bath by drawing a slow stream of dry air thru it while under diminished pressure -20 mm.

The ester was distilled under diminished pressure using a Wood's metal bath. It was found advantageous to use an ordinary Claisen distilling flask which had been modified with six pointed constrictions at the bend of the side neck as given by Noyes and Skinner. This prevented the ester from splashing over into the receiver.

Practically the entire product distilled over at 172-173° at 16 mm of mercury pressure; the metal bath stood at 205-210°. A small residue remained which could not be distilled over even by raising the temperature of the bath to 300°. The yield in every case equalled the original weight of the acid that was esterified or about 85% of the theory.

The ethyl ester of the dihydro b-naphtoic acid is a rather heavy greenish-yellow colored oily liquid with a specific gravity of 1.1155 at 20°; and 1.1126 at 25°. The refractive index (Zeiss refractometer) at 20° was found to be 1.5735; at 30° 1.5691 and at 35° 1.5665. Its boiling point at 16 mm of mercury pressure is 172°. The ester was found to be only moderately easily saponified and
yielded the original $^2$-dihydro b-naphtoic acid with a melting-point of 161° after refluxing with 30% potassium hydroxide for about four hours.

10. Condensation with Acetoacetic Ester

In the condensations of malonic ester and acetoacetic ester with $\alpha\beta$-unsaturated esters and ketones as used by Claisen$^{43}$, Michael$^{44}$, Auwers$^{45}$, Bredt$^{46}$, Knoevenagel$^{47}$, and Vorleander$^{48}$ the double bond was in an open chain compound. The condensation in this case is with an $\alpha\beta$-unsaturated ester in which the double bond is in the reduced naphthalene ring.

The condensation of the ethyl ester of the $^2$-dihydro b-naphtoic acid with acetoacetic ester was carried out in the usual way using sodium alcoholate as the condensing agent; the procedure followed was similar to that used by Rabe in his synthesis of phenanthrene. It was found, however, that if the sodium was used in greater than equivalent amounts there was some tendency to saponify the dihydro ester; this tendency was less when an exactly equivalent amount of sodium was used; and still less when there was less than the equivalent amount of sodium used.

A typical condensation which gave the best results was carried out by using

25 grams of ester
2.5 " of sodium
100 " of absolute alcohol
16.5 " of acetoacetic ester $\text{CH}_3\text{-C}^\equiv\text{CH}_2\text{-COOC}_2\text{H}_5$

The sodium was dissolved in the alcohol and the acetoacetic ester and the $^2$-dihydro b-naphtoic ester added; the mixture was then
refluxed upon an electric hot plate continuously for forty-eight hours. Extreme care was taken to prevent the entrance of moisture.

At the end of this time the reaction product was slightly acidified with sulfuric acid and the alcohol and acetoacetic ester distilled off on the hot water bath using a vacuum of 20 mm to 25 mm pressure. This left a heavy dark red colored liquid containing the unchanged ester and the condensation product, the 2,4 diketoctohydroanthracene 1-carboxylic ethyl ester.

For the separation of the latter advantage was taken of the fact that in its enol form it is acidic, whereas the dihydro b-naphtoic ester is not. The residue was treated with a dilute sodium carbonate—and in one case with sodium hydrogen carbonate solution and thoroughly shaken. After standing for a short time the sodium carbonate extract was thoroughly shaken out with ether to remove the unchanged ester; the sodium carbonate aqueous layer was then slightly acidified with sulfuric acid and the liberated ester extracted with ether. Upon evaporation of the ether a few crystals of a mixture of b-naphtoic acid and dihydro b-naphtoic acid crystallized out and were removed from the heavy dark red colored liquid which showed no tendency to crystallize. The liquid had a peculiar sweet odor and was considered to be the 2,4 diketoctohydroanthracene 1-carboxylic ethyl ester, since, as would be expected, there was probably a loss of alcohol and the formation of a closed ring as

\[
\begin{align*}
\text{H}_2\text{C}_8\text{C}_4\text{H}_4\text{C}_4\text{H}_4\text{C}_2\text{H}_5
\end{align*}
\]
From several typical condensations using 25 grams of the \( \Delta^2 \) dihydronaphthoic ester a total of slightly more than a half gram was obtained. One-tenth gram portions when dissolved in alcohol and titrated with tenth normal potassium hydroxide gave neutral equivalent values of 283.0, 278.0, and 276.0. The theoretical value for \( \text{C}_{17}\text{H}_{18} \text{O}_4 \) is 286.0.

It was thought that if the conditions of the reactions were varied somewhat the yield of the desired ester might be increased. When, however, the condensation was carried out using sodium in greater than equivalent amounts, practically none of the heavy red liquid product was obtained, but in place of it as much as three grams—using a 25 gram sample of the ethyl ester of \( \Delta^2 \) dihydronaphthoic acid,—of a solid acid which analysis showed to be a mixture of \( \Delta^2 \) dihydronaphthoic acid and naphthoic acid.

Two methods of preparing the 2,4 diketooctahydroanthracene were used. By the first a composite was made of the portions used for neutral equivalent titrations and two times the volume of tenth-normal potassium hydroxide that was used in their titration added. The mixture was gently refluxed for two or three hours and the alcohol evaporated off on the hot water bath. Dilute sulfuric acid was then added to slight acid reaction and the solution extracted with ether. The ether was allowed to evaporate at room temperature and then heated upon the hot water bath to expel carbon dioxide. The loss of carbon dioxide gave a product which formed a semi-crystalline mass which was easily soluble in ether, alcohol, sodium carbonate, and sodium hydrogen carbonate. This was considered to be the 2,4 diketooctahydro-
anthracene.

The second method, giving the same type of product, consisted of heating for eight to ten hours the diketoctohydroanthracene 1-carboxylic ethyl ester in a sealed tube with 1:1 hydrochloric acid. The tube was opened and the gases evolved were made to pass thru lime water; carbon dioxide was evolved in appreciable amounts. The contents of the tube were extracted with ether and the ether evaporated as in the former case. The product from both methods were subjected to distillation with zinc dust and gave the same results.

II. Distillation with Zinc Dust

The semi-crystalline mass containing the 2,4 diketoctohydroanthracene was thoroly mixed with zinc dust and distilled according to the instructions given by Noyes\textsuperscript{49}. A pyrex tube 10 mm in diameter and 85 centimeters long was fitted with a lose plug of asbestos about five or six inches from one end, then 5 cm of zinc dust was added, then the sample mixed with about 20 grams of zinc dust, then a mixture of zinc dust with about one-fourth its weight of asbestos and finally a lose plug of asbestos. The tube was rapped on the table so that a very distinct open channel remained above the entire charge. This was found necessary since there was quite a tendency for the zinc to expand when heated and fill the tube and prevent the easy passage of the hydrogen.

Hydrogen from a Kipp generator, purified by passing thru acid potassium permanganate, and sulfuric acid, was passed in at the end first filled until the air was expelled, a slow stream
was continued and the whole length of the tube containing the charge was heated in a combustion furnace to bright redness beginning first at the rear end. The yellow crystals of anthracene along with a very little oily material distilled out and condensed in the cool front end of the tube.

12. Identification of Anthracene

The crystals were scraped out and recrystallized from methyl alcohol. The methyl alcohol was found superior to benzene and toluene as a recrystallizing solvent for the anthracene, particularly because it is less soluble in the former and there is less tendency for the crystals to "creep". In all less than a tenth of a gram of recrystallized anthracene was obtained. The crystals were yellow in color and showed some fluorescence; after a second recrystallization they showed a melting point of 200°; mixed with pure anthracene the melting-point was 209°.

Several unsuccessful attempts were made to recrystallize and get a product which would melt correctly, but the nearest were always about two degrees (corrected) too low. In every mixed melting-point determination, however, the melting-point of the unknown material was raised by addition of pure anthracene.

The anthracene was further identified by oxidizing it with chromic acid in glacial acetic acid to anthraquinone. The anthraquinone upon a second recrystallization from methyl alcohol melted correctly at 273°; when mixed with pure anthraquinone there was no change in its melting-point. The apparent impurities which were not removed by recrystallization had been destroyed by oxidation.
IV: Summary

1. A derivative of anthracene was synthesized at temperatures below 100° by a series of reactions starting with naphthalene.
2. Attempts to condense 2,3 dibromotetrahydronaphthalene with malonic ester using sodium and magnesium alcoholate failed.
3. The $\Delta^2$ dihydro b-naphtoic acid was easily esterified with hydrochloric acid gas and absolute ethyl alcohol.
4. The ethyl ester of $\Delta^2$ dihydro b-naphtoic acid was condensed with acetoacetic ester by refluxing for several hours with less than the equivalent amount of sodium alcoholate.
5. The condensation product immediately loses alcohol giving 2,4 diketooctohydroanthracene 1-carboxylic ethyl ester, which was saponified with hydrochloric acid under pressure and with alcoholic potassium hydroxide. The acid obtained in the former case or by acidification with sulfuric acid in the latter lost carbon dioxide when heated upon the water bath giving 2,4 diketo-octohydroanthracene.
6. The 2,4 diketooctohydroanthracene yielded anthracene upon distillation with zinc dust. The anthracene was further identified by oxidation to anthraquinone.
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VI: Vita

The writer was born on a farm near Missouri Valley, Iowa February 28, 1885. He first went to school in McCook, Nebraska, attended other public schools in Nebraska and Iowa, and graduated from the Idaho Falls, Idaho high school in 1904. He received the Bachelor of Science degree from the University of Idaho in 1909; and the Master of Science degree from the same institution in 1911. He was Assistant Chemist of the Idaho Agricultural Experiment Station from 1907 to 1918. The publications of the writer are


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