

ever, can easily be isolated by forming the bisulfite addition compound and decomposing this with alkali or acid. B. p. 121°.

**Formation of Acrylic Acid.**—Four g. of aldehyde, 2.8 g. of potassium acetate and 24 cc. of acetic anhydride are boiled under a reflux condenser for 4 hours, water is added and the mixture evaporated to dryness. The residue is dissolved in sodium carbonate solution, the solution washed with ether and the acid precipitated by the addition of hydrochloric acid. Colorless crystals of *p*-diphenyl-acrylic acid are obtained. After recrystallization from 60% acetic acid, the material melts sharply at 184° and shows unsaturation when added to a potassium permanganate solution. No halogen could be detected. Molecular weight, 222; calc., 224.

**Preparation and Bromination of Ethyl Ester of *p*-Diphenyl-Acrylic Acid.**—1.5 g. acrylic acid is sealed in a tube with the calculated amount of absolute alcohol and sulfuric acid. This mixture is heated for 3 hours on the water-bath and then poured upon sodium carbonate. Yield 1.02 g. of ester. The ester is sealed in a tube with 2 atoms of bromine dissolved in carbon tetrachloride and after heating for 6 hours is entirely decolorized. The tube is opened and the carbon tetrachloride evaporated off. 0.75 g. of potassium hydroxide (10% excess) is added and the mixture heated on a water-bath, whereupon potassium bromide separates. The alcohol is evaporated off, water added, the solution filtered and acidified with dil. hydrochloric acid. The product may be recrystallized from 60% acetic acid. Crystals are obtained which melt between 145–147° with decomposition and evolution of carbon dioxide. The material contains no halogen, and is extremely unsaturated. Molecular weight, 222; calc., 222. The melting point after further recrystallization is 147°.

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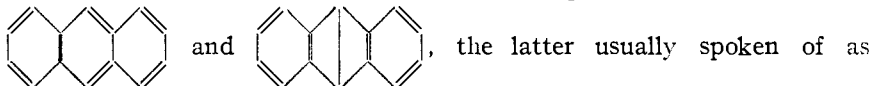
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

## SYNTHESIS OF ANTHRACENE<sup>1</sup> FROM NAPHTHALENE.

By C. W. COLVER, WITH WILLIAM A. NOYES.

Received January 10, 1921.

Since the discovery of anthracene in coal tar it has been prepared synthetically a great many times. A synthesis, however, from a derivative of naphthalene in which the naphthalene nucleus has been maintained intact has never been made. Such a synthesis would have considerable interest since it would explain satisfactorily the disposition of the fourth valence of the carbon atoms 9, 10, of anthracene. At the present time the two most common formulas which are given to anthracene are



the bridge formula. In some cases the experimental evidence seems to indicate that anthracene has the first formula and in others the results are explained just as well by either the first or second formula. Thus the reaction of aluminum chloride with tetrabromoethane in the presence of benzene to give anthracene is in favor of the

<sup>1</sup> An abstract of a thesis submitted by C. W. Colver in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of Illinois.

bridge structure, while the formation of anthracene by heating *o*-benzyltoluene in a red-hot tube or by passing its vapors over hot lead oxide and the elimination of all the bromine atoms and 2 hydrogen atoms from 2 moles of *o*-bromobenzyl bromide by heating it with sodium, may receive as satisfactory an explanation by one formula as by the other.

Centric and other formulas have been discussed by Bamberger,<sup>1</sup> Lagodzinski,<sup>2</sup> Armstrong,<sup>3</sup> Hewett<sup>4</sup> and others.

Berthelot<sup>5</sup> about 1870, when the interest in the study of anthracene was keenest, carried out a unique series of investigations by condensing acetylene with itself, with benzene, and with naphthalene to form such hydrocarbons as styrene, naphthalene, and anthracene. He passed a mixture of these various hydrocarbons through a red-hot tube at the rate of about one gram per minute, condensed the solid and liquid products and then subjected them all to analysis. In this way he was able to identify a large number of substances that were formed and to formulate a theory of their formation and structure.

Berthelot<sup>5</sup> considers that the formation of such hydrocarbons as styrene, naphthalene, and anthracene is due to the addition of one, two, or three equivalents of acetylene to one or two equivalents of benzene with or without the elimination of hydrogen. He points out particularly that naphthalene is formed "in large amounts when a mixture of benzene and acetylene is passed through a red-hot tube," and that styrene, naphthalene, and anthracene are not formed by a similar heating of pure benzene.

A considerable number of other syntheses of anthracene from benzyl chloride, phthalic anhydride, and other derivatives of benzene have been effected, but, so far as we can find, a synthesis from naphthalene has been effected only by Berthelot's pyrogenic reaction, just mentioned. That anthracene or a derivative of anthracene can be broken down to give naphthalene is made probable by the researches of Bamberger and Praetorius,<sup>6</sup> Dimroth and Schultze,<sup>7</sup> and Scholl and Zinke<sup>8</sup> who have oxidized anthraquinone derivatives to  $\alpha$ -naphthoquinones.

The present research had for its object the synthesis of anthracene from a derivative of naphthalene in which the actual nucleus of the naphthalene molecule was known to remain intact. This aim was not entirely realized but a derivative of naphthalene was prepared from which anthracene was obtained by distillation with zinc dust.

<sup>1</sup> Bamberger, *Ann.*, **257**, 1 (1890).

<sup>2</sup> Lagodzinski, *Ber.*, **27**, 1438 (1894).

<sup>3</sup> Armstrong, *Proc. Chem. Soc.*, **6**, 101 (1890).

<sup>4</sup> Hewett, *Z. physik. Chem.*, **34**, 17 (1900).

<sup>5</sup> Berthelot, *Ann.*, **142**, 251 (1867); *Bull. Soc. chim.*, **7**, 222 (1867); **7**, 279 (1867); **8**, 231 (1868); *Les Carbures d'Hydrogene*, **2**, 70-110 (1901).

<sup>6</sup> Bamberger and Praetorius, *Monatsh.*, **23**, 688 (1902).

<sup>7</sup> Dimroth and Schultze, *Ann.*, **411**, 339 (1916).

<sup>8</sup> Scholl and Zinke, *Ber.*, **51**, 1419 (1918); **52**, 1142 (1919).

### Experimental Part.

An unsuccessful attempt to synthesize anthracene from naphthalene was made in the first series of reactions which were carried out. Naphthalene was reduced to dihydro-naphthalene by a slight modification of the method given by Bamberger and Lodter.<sup>1</sup> The dihydro-naphthalene was then brominated in two ways: according to the method given by Bamberger and Lodter,<sup>2</sup> and by aspirating bromine vapors into a chloroform solution of the unsaturated compound. By the former method, the required amount of bromine dissolved in quite a large volume of chloroform was added to a chloroform solution of the dihydro-naphthalene while it was shaken and kept cold by a freezing mixture of salt and ice. This method gave fairly good yields, provided the bromination was attempted only in small lots not exceeding 2.5 g. If a 5- or 10-g. sample was used, the yield of dibromo-tetrahydro-naphthalene obtained was but very little if any more than would be obtained with a 2.5-g. sample.

The method of bromination which consists in aspirating bromine vapors into a chloroform solution of dihydro-naphthalene was found to be more successful. The required amount of bromine was weighed out in a brominating flask connected with a second flask surrounded by a freezing mixture and containing a chloroform solution of dihydro-naphthalene. The flask containing the bromine was warmed on a water-bath and then a slow stream of air was drawn through the apparatus to aspirate the bromine vapors. If the operation was carried out by addition of the bromine in the solvent, the brown color of the bromine was rapidly destroyed at first, but a little later the color disappeared much more slowly; if the bromine was introduced by aspirating it, then the brown color did not appear until just at the very end. The aspiration method of bromination gave yields approximating 80%, and 10- to 14-g. samples were brominated as successfully as a smaller one.

In order to attach two carbon atoms to the naphthalene molecule in each of the 3 and 4 positions, attempts were made to condense the dibromo-tetrahydro-naphthalene with malonic ethyl ester. Two procedures were used: the usual method with sodium and alcohol as the condensing agent, and with magnesium and alcohol as the condensing agent, a method used by Noyes and Kyriakides<sup>3</sup> for condensing ethylene bromide with malonic ester. Both methods of condensation, however, failed; in both cases the dibromo-tetrahydro-naphthalene was recovered unchanged.

In the second line of investigation, a ring of 4 carbon atoms was at-

<sup>1</sup> Bamberger and Lodter, *Ann.*, **288**, 74 (1895).

<sup>2</sup> *Ibid.*, **288**, 80 (1895).

<sup>3</sup> Noyes and Kyriakides, *THIS JOURNAL*, **32**, 1057 (1910).

tached to the 3 and 4 positions of the naphthalene molecule by a series of reactions which were suggested by the work of Rabe.<sup>1</sup> The ethyl ester of  $\Delta^2$ -dihydro- $\beta$ -naphthoic acid was prepared and condensed with aceto-acetic ester; the resulting ester was hydrolyzed and, with subsequent loss of carbon dioxide, gave 2-4 diketo-octohydro-anthracene which, upon distillation with zinc dust, gave anthracene.

**$\beta$ -Naphthalene Sulfonic Acid.**—This acid was prepared by sulfonation of naphthalene according to the method of Witt.<sup>2</sup> Better yields were obtained and less time was required to carry out the operation when the naphthalene was heated to 160° in an oil-bath and stirred constantly with an efficient mechanical stirrer during the addition of the sulfuric acid. The  $\beta$ -naphthalene sulfonic acid crystallizes as the trihydrate, and these crystals were best separated from the mother liquor and recrystallizing solvent of dil. hydrochloric acid by means of a centrifuge. Filtration with a cloth did not prove successful since the crystals stuck together in such a way that the mother liquor was sucked off with great difficulty. The acid was obtained in yields of about 70%.

**$\beta$ -Naphthonitrile.**—To prepare the nitrile, the sodium salt of  $\beta$ -naphthalene sulfonic acid was distilled with potassium ferrocyanide, according to the method of Derick and Kamm,<sup>3</sup> and with sodium cyanide. The best yields were obtained by distilling small amounts of a mixture of equal parts of the sodium salt and finely ground sodium cyanide from an iron retort under diminished pressure of 30 to 60 mm. 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.

The first type of apparatus consisted of a 25 mm. iron pipe 46 cm. 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 6 mm. pipe, 20 cm. long, was screwed. To this outlet-pipe a 61-cm. 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 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 lighted 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.

The second type of retort consisted of a 38 mm. pipe, 20 cm. long, fitted with caps and a 6 mm. outlet-pipe 20 cm. long. This outlet-pipe was bent so that the retort could be used in a position inclined at an angle of about 45° from the horizontal. The apparatus was charged with 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 tube was made to dip just into a small amount of water in the receiver so that the nitrile 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 to 50%.

**$\beta$ -Naphtholic Acid.**—The crude nitrile was hydrolyzed to the acid without further purification. The procedure given by Baeyer and Besemfelder<sup>4</sup> of refluxing with an equal mixture of conc. sulfuric acid, glacial acetic acid, and water was used in a few

<sup>1</sup> Rabe, *Ber.*, 31, 1896 (1898).

<sup>2</sup> Witt, *ibid.*, 48, 743 (1915).

<sup>3</sup> Derick and Kamm, *THIS JOURNAL*, 38, 400 (1916).

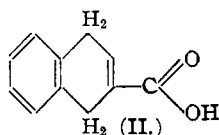
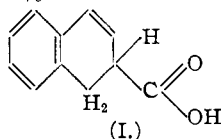
<sup>4</sup> Baeyer and Besemfelder, *Ann.*, 266, 187 (1891).

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. It was found preferable to hydrolyze the nitrile by refluxing it with a 20 to 30% solution of potassium hydroxide for about 6 to 8 hours and since the reaction could easily be carried to completion and the danger of charring was entirely avoided; thus, a product was obtained which was easily purified without the use of boneblack and repeated recrystallizations.

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 filtered through a thick pad of asbestos, diluted and the  $\beta$ -naphthoic acid precipitated by adding conc. hydrochloric acid. The acid was filtered with suction, washed, dissolved in dil. potassium hydroxide solution and again precipitated with hydrochloric acid. In this second precipitation it was found that if approximately 1 *N* 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  $\beta$ -naphthoic acid. The yields of  $\beta$ -naphthoic acid were 20% of the amount calculated, on the basis of the sulfonic acid used.

**$\Delta^2$ -Dihydro- $\beta$ -Naphthoic Acid.**—The  $\beta$ -naphthoic acid was reduced with 3% sodium amalgam according to the method of Baeyer and Besemfelder.<sup>1</sup> The progress of the reduction was determined by removing small samples (0.5 cc.) at regular intervals and testing them with potassium permanganate as recommended by Derick and Kamm.<sup>2</sup> Complete reduction was effected in about an hour and a half. Reduction in the cold according to this procedure yields about 75% of the labile  $\Delta^3$ -dihydro-naphthoic acid (I) and 25% of the stable  $\Delta^2$ -dihydro-naphthoic acid (II). In this work, however,



only the  $\Delta^2$  isomer was desired, so after separation of the mercury and careful filtration through an asbestos pad, a small amount of sodium hydroxide was added and the solution was heated on the water-bath for an hour and a half to rearrange the labile into the stable form.

The stable and labile isomers were precipitated with hydrochloric acid, purified, and successfully separated from each other by fractional precipitation. One reduction gave 10 fractions which, without recrystallization, gave melting points as follows: Fractions 1-5, 156-157°; Fraction 6, 156-158°; Fraction 7, 152-155°; Fraction 8, 120-121°; Fraction 9, 100°; Fraction 10, 99°.

These fractions were about equal in amount and therefore show that about 70% of the product was the stable  $\Delta^2$  isomer, 10% a mixture of the two forms, and 20% the labile  $\Delta^3$  isomer. The correct melting point of the stable acid is 161°; for the labile, 101.2°. The yield of the recrystallized  $\Delta^2$  dihydro- $\beta$ -naphthoic acid was about 65%.

**Ethyl Ester of  $\Delta^2$ -Dihydro- $\beta$ -naphthoic Acid.**—The  $\Delta^2$ -dihydro- $\beta$ -naphthoic acid

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Derick and Kamm, *loc. cit.*

was esterified according to the method of Fischer and Speier.<sup>1</sup> The acid was dissolved in absolute alcohol, dry hydrogen chloride run in and the mixture refluxed for about 6 hours. The larger part of the excess alcohol was distilled under reduced pressure (20 mm.) and the remainder of the solution was poured into 4 or 5 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. Upon acidification, the aqueous layer gave only a small precipitate of dihydro acid which showed that the esterification had been almost complete. The ether layer was transferred to a Claisen distilling flask, 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 through it while under 20 mm. pressure.

The ester was distilled under diminished pressure. A Wood's-metal-bath was used. To prevent the ester from splashing over into the receiver, it was found advantageous to use an ordinary Claisen distilling flask which had been modified with 6 pointed constrictions at the bend of the side neck as given by Noyes and Skinner.<sup>2</sup> Practically the entire product distilled at 172° to 173° under a vacuum of 16 mm. The metal-bath stood at 205° to 210°. A small residue remained which could not be distilled even by raising the temperature of the bath to 300°. The yield of the ester was about 85%.

The ethyl ester of the  $\Delta^2$ dihydro- $\beta$ -naphthoic acid is a rather heavy greenish-yellow colored oily liquid;  $d^{20}$ , 1.1155;  $d^{25}$ , 1.1126;  $n_D^{20}$ , 1.5735,  $n_D^{30}$ , 1.5691;  $n_D^{35}$ , 1.5665 Zeiss refractometer; b. p. 172° (16 mm.). The ester was saponified with some difficulty but yielded the original  $\Delta^2$ dihydro- $\beta$ -naphthoic acid with a melting point of 161° after refluxing it with 30% potassium hydroxide solution for about 4 hours.

**Condensation with Aceto-acetic Ester.**—In the condensations of malonic ester and aceto-acetic ester with  $\alpha,\beta$ -unsaturated esters and ketones as carried out by Claisen,<sup>3</sup> Michael,<sup>4</sup> Auwers,<sup>5</sup> Brecht,<sup>6</sup> Knoevenagel,<sup>7</sup> and Vorländer,<sup>8</sup> 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  $\Delta^2$  dihydro- $\beta$ -naphthoic acid with aceto-acetic 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<sup>9</sup> 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.

A typical condensation which gave the best results was carried out by using 25 g. of ester, 2.5 g. of sodium, 100 g. of absolute alcohol, 16.5 g. of aceto-acetic ester. The sodium was dissolved in the alcohol and the aceto-acetic ester and the  $\Delta^2$ -dihydro-

<sup>1</sup> Fischer and Speier, *Ber.*, **28**, 3252 (1895).

<sup>2</sup> Noyes and Skinner, *THIS JOURNAL*, **39**, 2718 (1915).

<sup>3</sup> Claisen, *J. prakt. Chem.*, N. F. **35**, 413 (1887).

<sup>4</sup> Michael, *ibid.*, **35**, 349 (1887); **43**, 390 (1891); **45**, 55 (1892); **49**, 20 (1894); *Ber.*, **27**, 2126 (1894).

<sup>5</sup> Auwers, *ibid.*, **24**, 307 (1891); **28**, 1130 (1895).

<sup>6</sup> Brecht, *ibid.*, **24**, 603 (1891).

<sup>7</sup> Knoevenagel, *ibid.*, **26**, 1085 (1893); **27**, 2337 (1894); **29**, 172 (1896); *Ann.*, **281**, 25 (1894).

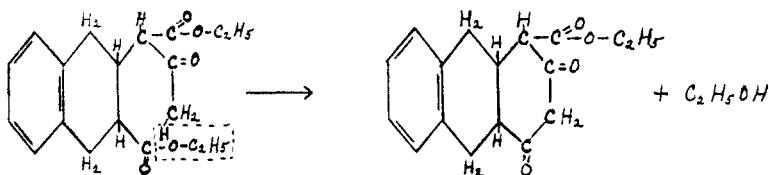
<sup>8</sup> Vorländer, *Ber.*, **27**, 2053 (1894); *Ann.*, **294**, 253 (1896).

<sup>9</sup> *Loc. cit.*

$\beta$ -naphthoic ester added; the mixture was then refluxed upon an electric hot plate continuously for 48 hours. Extreme care was taken to prevent the entrance of moisture.

At the end of this time the reaction product was acidified slightly with sulfuric acid and the alcohol and aceto-acetic ester distilled with the aid of a hot-water bath and a pressure of 20 to 25 mm. This left a heavy dark-red colored liquid containing the unchanged ester and the condensation product—2,4-diketo-octohydro-anthracene-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  $\Delta^2$  dihydro- $\beta$ -naphthoic ester is not. The residue was treated with a dil. sodium carbonate solution (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 with ether to remove the unchanged ester; then the aqueous layer containing sodium carbonate was acidified slightly with sulfuric acid and the liberated ester extracted with ether. Upon evaporation of the ether a few crystals of a mixture of  $\beta$ -naphthoic acid and  $\Delta^2$  dihydro- $\beta$ -naphthoic acid formed and were removed from the heavy dark-red colored liquid, which showed no tendency to crystallize. The liquid, which had a peculiar sweet odor, was 2,4-diketo-octohydro-anthracene-1-carboxylic ethyl ester, since, as would be expected, there was probably a loss of alcohol and the formation of a closed ring as



From several typical condensations with a 25-g. portion of the  $\Delta^2$ dihydro- $\beta$ -naphthoic ester a total of slightly more than 0.5 g. of this ester was obtained. 0.1 g. portions, when dissolved in alcohol and titrated with 0.1 *N* potassium hydroxide solution, gave neutral equivalent values of 283.0, 278.0, and 2.76. The calculated value for  $C_{17}H_{16}O_4$  is 286.

It was thought that if the conditions of the reaction were varied somewhat the yield of the desired ester might be increased. When, however, the condensation was carried out with sodium in greater than equivalent amounts, practically none of the heavy red liquid product was obtained, but in place of it as much as 3 g. (using a 25-g. sample of the ethyl ester of  $\Delta^2$ dihydro- $\beta$ -naphthoic acid) of a solid acid which analysis showed to be a mixture of  $\Delta^2$ dihydro- $\beta$ -naphthoic acid and  $\beta$ -naphthoic acid.

Two methods were used for preparing the 2,4-diketo-octohydro-anthracene. In the first, a composite was made of the portions used for neutral equivalent titrations and twice the volume of 0.1 *N* potassium hydroxide solution employed in their titration was added. The mixture was refluxed gently for 2 or 3 hours and the alcohol evaporated on the water-bath. Dil. 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 water-bath to expel carbon dioxide. The loss of carbon dioxide gave the 2,4-diketo-octohydro-anthracene as a semi-crystalline mass which was easily soluble in ether, alcohol, sodium carbonate, and sodium hydrogen carbonate.

In the second method which gives the same type of product the diketo-octohydro-anthracene-1-carboxylic ethyl ester was heated for 8 to 10 hours in a sealed tube with 1:1 hydrochloric acid. The tube was opened and the gases evolved were made to pass through 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 products from the two methods were subjected to distillation with zinc dust; each gave the same result.

**Distillation with Zinc Dust.**—The semi-crystalline mass of 2,4-diketo-octohydro-anthracene was thoroughly mixed with zinc dust and distilled according to the instructions given by Noyes.<sup>1</sup> Yellow crystals of anthracene along with a very little oily material distilled and condensed in the cool front end of the tube.

**Identification of Anthracene.**—The crystals were scraped out of the tube and recrystallized from methyl alcohol. The methyl alcohol was found superior to benzene and toluene as a crystallizing solvent for anthracene, particularly because it is less soluble in the former and there is less tendency for the crystals to "creep." In all less than 0.1 g. 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 obtain by recrystallization a product which would melt correctly, but the nearest melting points were always about 2° (corr.) 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 to anthraquinone with chromic acid in glacial acetic acid. 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. Apparently the impurities which were not removed by recrystallization had been destroyed by oxidation.

### Summary.

1. A derivative of anthracene was synthesized at temperatures below 100° by a series of reactions starting with naphthalene.
2. Attempts failed to condense 2,3-dibromo-tetrahydro-naphthalene with malonic ester, using either sodium or magnesium alcoholate.
3.  $\Delta^2$ dihydro- $\beta$ -naphthoic acid was easily esterified with hydrogen chloride and absolute ethyl alcohol.
4. The ethyl ester of  $\Delta^2$ dihydro- $\beta$ -naphthoic acid was condensed with aceto-acetic ester by refluxing it for several hours with less than the equivalent amount of sodium alcoholate.
5. The condensation product immediately loses alcohol to give 2,4-diketo-octohydro-anthracene-1-carboxylic ethyl ester, which was saponified with hydrochloric acid under pressure and with alcoholic potassium hydroxide solution. The acid obtained in the former case and by acidification with sulfuric acid in the latter lost carbon dioxide when heated upon the water-bath, giving 2,4-diketo-octohydro-anthracene.
6. The 2,4-diketo-octohydro-anthracene yielded anthracene upon distillation with zinc dust. The anthracene was identified by its melting point and by oxidation to anthraquinone.
7. Since this synthesis was effected with a derivative of dihydro-naphthalene and not with naphthalene itself, no evidence has been obtained upon the question of a *para* union in the central nucleus of anthracene.

<sup>1</sup> Noyes, "Organic Chemistry for the Laboratory," 1920, p. 60.