

SYNTHESIS OF BENZO [a] PHENANTHRENE  
AND RELATED COMPOUNDS

by

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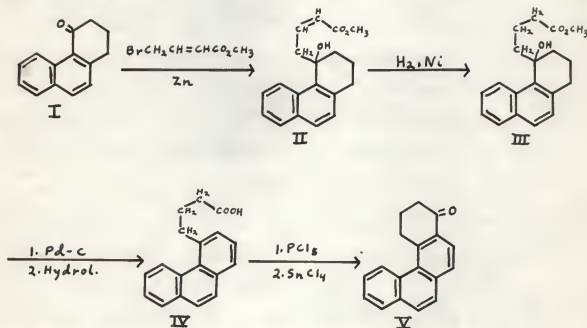
## INTRODUCTION

The discovery, in recent years, of polynuclear compounds of physiological and medical interest, particularly steroids, carcinogenic agents, and related compounds, has led to a stimulation of research into methods and procedures for the preparation of polynuclear compounds. Methods of chain attachment, chain lengthening, and ring formation have all come under study, and in many cases have resulted in new and improved procedures, or a decided increase in yield of a polynuclear compound or of its intermediates. A good deal of this work has centered around compounds related to phenanthrene, such as various substituted cyclopentanoperhydrophenanthrenes (steroid precursors) and substituted benz- and di-benz-phenanthrenes. The latter series of compounds, because of the carcinogenic properties of some of its members, has been the subject of considerable synthetic study.

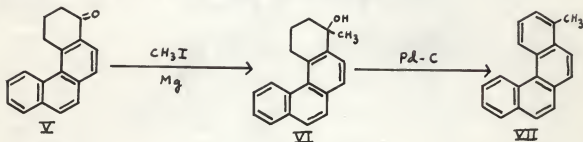
Of interest in the present work is the benzo [c] phenanthrene nucleus, or more particularly the ketone, 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene. Because of its value as an intermediate in the preparation of benzo- [c] phenanthrene derivatives and of higher condensed hydrocarbons it would be desirable to have a straight forward synthesis of this ketone starting from compounds which are easily prepared and readily available. In line with this the present investigation had two objectives: (1) the development of a shorter, more efficient route to 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, and (2) the preparation from this intermediate of 4-methylbenzo [c] phenanthrene and of derivatives leading towards the synthesis of the hitherto unreported hydrocarbon, benz [1] acephenanthrylene. The preparation of 4-methylbenzo [c] phenanthrene was desired as a proof of structure of the ketone and also for yield comparisons with

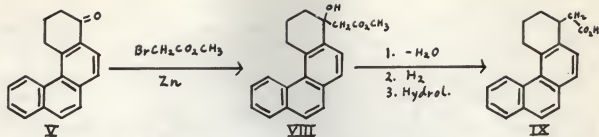
other syntheses of this hydrocarbon.

To accomplish the first of these objectives it was proposed to carry out a Reformatsky type of condensation between methyl  $\gamma$ -bromocrotonate and 4-keto-1,2,3,4-tetrahydronaphthalene. The former ester is readily available through the allylic bromination of methyl crotonate with *N*-bromosuccinimide and the latter ketone is easily prepared from naphthalene by well known procedures. Starting with this reaction the proposed synthesis would proceed in four steps:

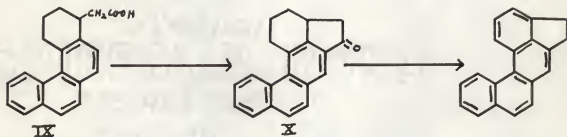


With the four-ring ketone as an intermediate the additional conversions would be carried out in two different directions:



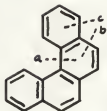


Compound IX has not been reported previously. A suitable cyclization of this acid should produce the ketone X, 1,2,3,3a,4,5-hexahydrobenz [1] acephenanthrylene, which upon reduction and dehydrogenation would lead to the five-ring hydrocarbon, benz [1] acephenanthrylene.



#### HISTORY

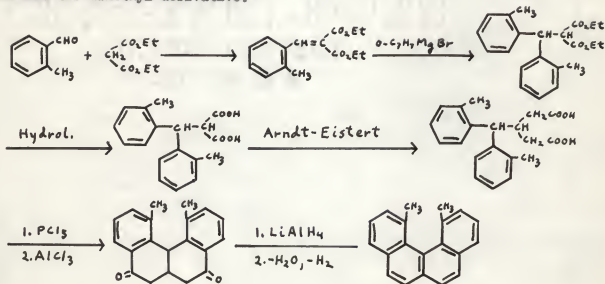
Research on the preparation of polynuclear compounds has resulted in a number of independent synthesis of benzo [c] phenanthrene and its alkyl derivatives. These methods have been summarized by Bergmann and Szmujskovicz (7) according to whether ring closure has proceeded along lines a, b, or c of the diagram:



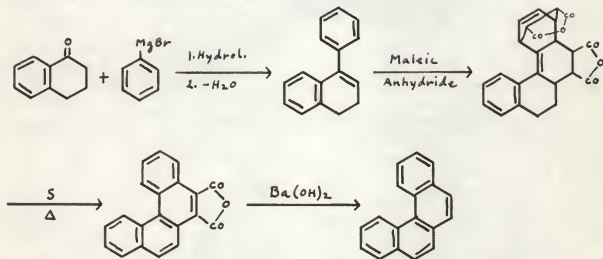
The respective ring closures were carried out with  $\alpha$ -(2-naphthyl)- $\beta$ -(*o*-aminophenyl)-acrylic acid, (Cook, 8) (Pshorr synthesis, line a); 1-phenyl-

tetralin-2-acetic acid, (Hewett, 13) (line b);  $\gamma$ -(4-phenanthryl) butyric acid, (Bachman and Edgerton, 4) (line c); and 2-( $\beta$ -phenethyl)-1-tetralol, (Ganguly, 12) (line a). In all of these cases the over-all yield of the benzo [c] phenanthrene nucleus was small and the procedures were rather drawn out. All six of the mono-methyl derivatives of benzo [c] phenanthrene have been prepared and tested for carcinogenic activity. The 5- and 6-methyl compounds have been found to be particularly active. (13,15). Five of these isomers were first prepared by Hewett. This investigator prepared the 5-methyl derivative by an adaptation of the second ring closure cited above (13). The 2-, 3-, and 4- methyl-derivatives were prepared through a procedure similar to the Pschorr synthesis, in which ring closure proceeded through an o-halogen instead of an o-amino group (Hewett, 14). The 6-methyl derivative was prepared by a Wolff-Kishner reduction of 3,4-benz-1-phenanthraldehyde prepared by the same type of synthesis (Hewett, 15).

Recently, two interesting syntheses of the benzo-[c] phenanthrene nucleus have been developed by Newman and Wolf (19) and by Szmuszkowicz and Modest (22). In the former case a double ring closure was effected to produce the dimethyl derivative:



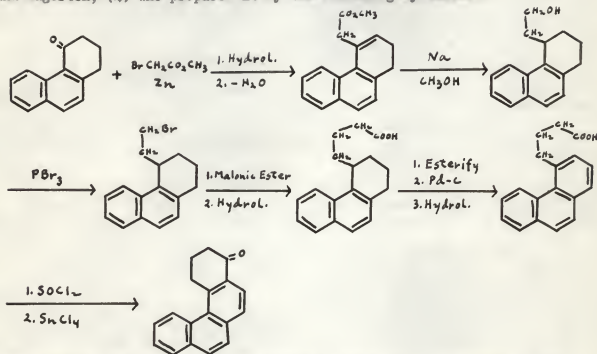
The synthesis proceeded in good yield except for the final dehydrogenation-dehydration of the diol to the hydrocarbon (19 percent). Indeed the over-all yield of the hydrocarbon from 2,2'-dimethylbenzhydrylmalonic acid was only 4 percent. The synthesis proved adaptable also for the preparation of the 1-methyl and 1,5,8,12-tetramethyl derivatives. The aromatizations proceeding somewhat better in these cases (34 percent and 45 percent) to give over-all yields from the analogous malonic acids of 10 percent and 3 percent respectively. In the synthesis of Szmuszkowicz and Modest (22), which represents the present simplest and most efficient procedure, use is made of a Diels-Alder addition of maleic anhydride to alkyl-substituted 1-phenyl-3,4-dihydronaphthalenes:



This synthesis has been repeated on a larger scale by Newman, et. al. (20) for the production of investigative quantities of benzo [c] phenanthrene and its six monomethyl derivatives. Over-all yields of 15-20 percent were obtained for the final hydrocarbons.

While the latter synthesis is obviously the simplest and most direct route to the hydrocarbons themselves, it cannot be used for the preparation of ketone intermediates containing the benzo [c] phenanthrene nucleus. These

ketones are valuable in the synthesis of higher condensed systems, and for the preparation of carbinols, acids and esters through condensation reactions. The more classical method of ring closure, involving cyclization of aryl-substituted acid chlorides, still offers the best route to these reactive intermediates, and has been used in a number of cases. The only previous report of 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene was by Bachmann and Edgerton, (4) who prepared it by the following synthesis:

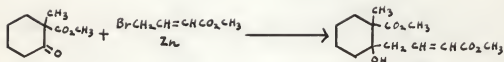


The procedure was lengthy and the over-all yield low (10 percent). The same general method of synthesis was followed more recently by Newman and Wheatley (18) in their preparation of the previously unreported 1-methylbenzo [c] phenanthrene. Methyl- $\alpha$ -bromopropionate was used in the Reformatsky condensation and chain lengthening was carried out through the Arndt-Eistert synthesis to give  $\gamma$ -(4-phenanthryl) valeric acid. Cyclization of this acid produced 1-methyl-4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, which upon reduction, dehydration and dehydrogenation gave the desired hydrocarbon. The over-all yield was practically the same in this case, (11 percent).



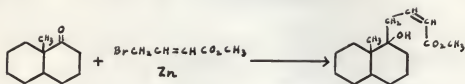
As was found in the Bachmann-Edgerton (4) synthesis,  $\gamma$ -(4-phenanthryl) butyric acid is readily cyclized in good yield to 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene (85-95 percent). The elimination of the tedious chain-lengthening steps from the synthesis of this acid was, therefore, the logical point of attack in the present investigation. The most efficient way to accomplish this would of course be the direct attachment of a four-carbon chain to 4-keto-1,2,3,4-tetrahydrophenanthrene. For this synthesis methyl  $\gamma$ -bromocrotonate is admirably suited. This valuable reagent, which is readily prepared by the method of Ziegler, et. al. (23) has found increasing use in recent years, particularly in the synthesis of steroid intermediates. The use of this halo ester in the Reformatsky reaction has, with some exceptions, been found to give lower yields than the  $\alpha$ -halo esters which are used normally. However, lower yields are more than compensated for by the convenience of direct attachment of a four-carbon chain.

Some recent examples of this type of reaction may be cited. Bachmann and Dreiding (3) reacted 2-methyl-2-carbomethoxycyclohexanone with methyl  $\gamma$ -bromocrotonate to produce the methyl ester of  $\gamma$ -2-methyl-2-carboxy-1-hydroxycyclohexanecrotonic acid:



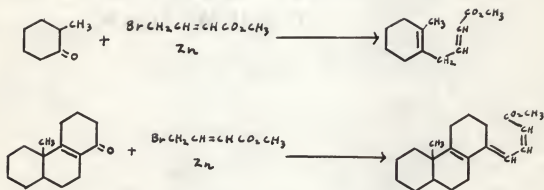
The product was fractionated under vacuum without loss of water to give an exceptionally high yield of the hydroxy ester (84 percent). This ester was hydrogenated and hydrolysed to give the hydroxy acid in 68 percent yield.

However, treatment of the same ester with thionyl chloride, followed by hydrolysis, gave the diene acid in 82 percent yield. Thus there seemed to be some indication of alkaline cleavage of the hydroxy ester. In another reaction *cis*-9-methyl-1-decalone was treated with methyl bromocrotonate to give methyl 9-methyl-1-hydroxy-1-*cis*-decalinercrotonate:



In this case the product contained considerable unreacted ketone and distilled with some decomposition. The product was hydrogenated, dehydrated with anhydrous potassium sulphate, and hydrolyzed. The recovered unreacted ketone indicated a yield of 61 percent of the Reformatsky ester.

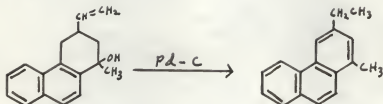
Cook and Philip (9) in similar experiments obtained the diene esters directly, as indicated in the following equations:



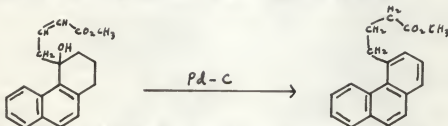
Yields here were in the neighborhood of 50-60 percent. The determining factor in the production of hydroxy ester or diene ester, while influenced partly (as above) by opportunities for conjugation, probably lies largely in the conditions under which the reaction is carried out. Among the more

important of these conditions is the type of solvent. Bachmann and Dreiding used a 50-50 mixture of ether-benzene, whereas Cooke and Philip used benzene alone. The lower reflux temperature of the ether-benzene mixture probably tends to prevent dehydration. The amount of solvent used also seems to have some bearing on the course of the reaction. This will be discussed more fully in connection with the present investigation.

The possibility of carrying out a simultaneous dehydration, and hydrogenation-dehydrogenation has been demonstrated by Bachmann and Struve (5) who carried out the conversion:



By analogy it seemed logical that a similar type of conversion would be successful with the unsaturated Reformatsky esters obtained with methyl bromocrotonate, leading directly to aryl butyric esters:



Although results obtained in the present investigation proved disappointing (see experimental) such a triple reaction may be successful in other cases.

## EXPERIMENTAL

Preparation of  $\beta$ -Naphthoylpropionic Acid

Twenty-five grams (0.25 mole) of succinic anhydride was added to a solution of 60 g. (0.45 mole) of anhydrous aluminum chloride in 190 ml. of reagent grade nitrobenzene. When all solid material was in solution, the mixture was cooled in an ice bath and 45 g. (0.35 mole) of naphthalene was added gradually, with constant swirling. A dark-red complex formed and the mixture was allowed to stand, with occasional swirling, for at least 12 hours. The mixture was again cooled in an ice bath and the complex decomposed by the addition of ice.

In a typical purification five of the above reaction mixtures were combined and subjected to steam distillation to remove nitrobenzene. The solid residue was washed with water, dissolved in 1000 ml. of 10 percent sodium carbonate, and again steam distilled. The alkaline solution was filtered to remove aluminum salts and the mixture of  $\alpha$ - and  $\beta$ -isomers was precipitated with 1:1 hydrochloric acid. The crude acids were filtered, washed and dried. The mixture of  $\alpha$ - and  $\beta$ -isomers was redissolved in a slight excess of sodium hydroxide and made up to a volume of three liters. Fractional precipitation of the two isomers was effected by successive additions to the hot solution of one-fifth the molar amount of 2*N* hydrochloric acid necessary for complete neutralization, followed by cooling and filtration after each precipitation. By this method a 30-35 percent yield of the  $\beta$ -isomer was obtained. Precrystallization from acetic acid gave pure  $\beta$ -naphthoylpropionic acid; mp. 171-172° C. uncorr.

Preparation of  $\gamma$ -(2-Naphthyl)butyric Acid

A mixture of 40.5 g. (0.13 mole) of  $\beta$ -naphthoylpropionic acid, 60 ml. water, 138 ml. con. hydrochloric acid, 80 ml. of toluene, and 100 g. of amalgamated zinc (prepared by treating 95 g. mossy zinc with 9.5 g. mercuric chloride dissolved in 160 ml. water and 5.5 ml. con. hydrochloric acid) was placed in a one-liter, round-bottom flask. The mixture was refluxed vigorously for 30 hours, with addition of three 40 ml. portions of concentrated hydrochloric acid during this period. The toluene layer was separated and cooled in ice water to give 30.7 g. of crystalline product. The aqueous layer was extracted with benzene and the benzene added to the toluene filtrate. The combined solvent was removed under reduced pressure giving a second crop of 4.0 g. of crystals for a total of 34.7 g. crude product (91 percent). Recrystallization of the product from benzene, followed by a petroleum ether-benzene wash gave lustrous plates of pure  $\gamma$ -(4-naphthyl)butyric acid; mp.  $96^{\circ}$ - $98^{\circ}$  C. uncorr.

## Preparation of 4-Keto-1,2,3,4-tetrahydrophenanthrene

The procedure of Bachmann and Cortes (2) was followed in this preparation. Eighteen grams (.087 mole) of phosphorus pentachloride was added slowly, with swirling, to a solution of 14.4 g. (.067 mole) of  $\gamma$ -(2-naphthyl)butyric acid in 100 cc. of benzene. The mixture was allowed to stand for one hour with occasional swirling, and then cooled in an ice bath. The mixture was cooled and 15 ml. of anhydrous stannic chloride was added slowly with constant swirling. A bright orange complex was formed and the mixture became quite viscous. The mixture was allowed to stand for 20 minutes and

then poured into a slurry of ice and dilute hydrochloric acid. The organic layer was washed twice with dilute hydrochloric acid, twice with water, three times with five percent sodium bicarbonate solution, and twice more with water. The benzene solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was subjected to vacuum distillation and gave 12.1 g. (91 percent ) of distilled product. Recrystallization from methyl alcohol-acetone gave colorless rhombs; mp. 66.5-67.5° C. uncorr.

Preparation of Methyl  $\gamma$ -[4-(4-hydroxy-1,2,3,4-tetrahydrophenanthryl)]Crotonate

A mixture of 4.2 g. (.021 mole) of 4-keto-1,2,3,4-tetrahydrophenanthrene dissolved in 100 ml. of anhydrous benzene was introduced into a 500 ml., three-neck, round bottom flask equipped with condenser, stirring motor and dropping funnel. Methyl  $\gamma$ -bromocrotonate, 11.3 g. (.063 mole), prepared by the method of Ziegler, (23) was dissolved in 25 ml. anhydrous benzene and introduced into the dropping funnel. One-fourth of the bromocrotonate solution was run into the flask together with 10 g. of 40 mesh zinc (cleaned with dilute hydrochloric acid, rinsed with water and acetone, and dried). The vigorously stirred mixture was heated in an oil bath, and a few crystals of iodine were added to start the reaction. After about five minutes the reaction began, caused the solution to become cloudy, white, then yellow as more of the complex formed. The remainder of the bromocrotonate solution was dropped in slowly during the course of one hour. Refluxing and stirring were continued for an additional three hours. At one-half hour intervals five gram portions of fresh zinc were added together with one or two crystals of iodine.

The bright-yellow complex, which had become quite thick, was dissolved in 50 ml. of glacial acetic acid, and poured into a mixture of ice and dilute hydrochloric acid. The flask was rinsed with ether and acetic acid and the washings added to the main extract. The organic layer was separated and in succession washed with dilute hydrochloric acid, cold water, 1 percent ammonia, and finally with water again until the washings were neutral to litmus. The solution was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The residue was heated under vacuum on a hot water bath at 80-90° for one hour to remove volatile impurities. The residue, 7.5 g., was a reddish-yellow, sweet smelling, viscous oil.

The crude Reformatsky product (mixed with unreacted ketone) proved to be unstable in purification procedures. Vacuum distillation converted the material into a nonvolatile, dark-red viscous polymer at pot temperatures over 200°. Only unreacted ketone was recovered in the distillate. Upon saponification, the crude ester cleaves to a large extent to give the original 4-keto-1,2,3,4-tetrahydrophenanthrene (identified through its melting point and that of its 2,4-dinitrophenylhydrazone). As a result, no further purification was carried out on the crude Reformatsky residue, and it was used directly for further experiments.

Attempted Conversion of the Crude Reformatsky Ester  
Directly to  $\gamma$ -(4-Phenanthryl)butyric Acid

A mixture of 0.5 g. of the crude Reformatsky product with 0.05 g. of 30 percent palladium-charcoal was heated at 300-320° for five minutes, during which time only a small evolution of gas was observed. The mixture was extracted with benzene, the solvent was removed, and the residue saponified with 50 ml. of 10 percent potassium hydroxide-methanol. Removal of excess

methanol, extraction of non-saponifiable materials, and acidification gave a brown-black tarry material which did not crystallize upon standing. A similar experiment in which naphthalene was used as a diluent and hydrogen acceptor gave the same results.

Preparation of Methyl  $\gamma$ -[4-(4-hydroxy-1,2,3,4-tetrahydrophenanthryl)]butyrate

A solution of 7.5 g. of the crude Reformatsky product in 50 ml. of cold methyl alcohol was filtered from a small amount of undissolved ketone. The solution was boiled with Norite, filtered, and diluted to 80 ml. with methyl alcohol. Raney nickel catalyst (5 g.) was added and the mixture was hydrogenated at 40 psi and 22° for two hours. At the end of this period the solution gave a negative unsaturation test. The catalyst was filtered, the solvent removed, and the residue distilled under vacuum. There was obtained 3.8 g. of clear, colorless, very viscous distillate. Assuming this to be the pure saturated hydroxy ester the yield based on 4-keto-1,2,3,4-tetrahydrophenanthrene was 62 percent.

Preparation of  $\gamma$ -(4-Phenanthryl)butyric Acid

Directly from Crude Saturated Ester. A portion of the methanolic solution of the saturated Reformatsky ester from the hydrogenation procedure was evaporated to dryness. The residue of 1.4 g. which remained, was dehydrogenated with 0.2 g. of 10 percent palladium-charcoal in a nitrogen-flushed apparatus at 315-325° for 45 minutes. Evolution of gas, which was fairly rapid during the first five minutes, was observed. The mixture was extracted with benzene, filtered, and the solvent was removed. The residue was saponified by refluxing for two hours in a mixture of 50 ml. methanol



and 10 g. potassium hydroxide. Excess methanol was removed, the solution was diluted with water and non-saponifiable material was extracted with ether. Acidification of the alkaline solution followed by ether extraction and removal of the solvent gave a brown gum. The gum was dissolved in 5 percent sodium bicarbonate solution, again extracted with ether, and filtered. Upon acidification a brown gum, which became crystalline upon standing for several hours, again separated. The crude  $\gamma$ -(4-phenanthryl) butyric acid (mp. 136-139° uncorr.) amounted to 0.38 g. or a yield of 35 percent based on the starting ketone.

From Saturated Ester Purified by Saponification and Re-esterification. The remainder of the saturated Reformatsky ester from the above experiment was diluted to 50 ml. with methanol and 5 g. of potassium hydroxide was added. The mixture was refluxed for two hours, excess methanol was removed, and the solution diluted with water. Non-saponifiable material was extracted with ether and the alkaline solution was acidified. Extraction of the acidified mixture with ether and removal of solvent gave a brown oil which was re-esterified by refluxing for three hours with a mixture of 50 ml. methanol and 5 ml. of concentrated sulfuric acid. The solvent was removed, the solution was diluted with water and the ester was extracted with ether. The extract was dried over anhydrous magnesium sulfate and the solvent removed to give a brown, oily residue weighing 2.4 g.

The ester residue was dehydrogenated over 0.3 g. of 10 percent palladium-charcoal in a nitrogen-flushed apparatus at 325-355° for two hours. Hydrogen (0.01 mole) was liberated, or slightly more than the theoretical amount, assuming the residue to be pure hydroxy ester. The dehydrogenated material was extracted, hydrolyzed and the crude acid was obtained by the

same procedure as in the preceding experiment. Acid (0.9 g.) was obtained (mp. 137-139° uncorr.), or a 16 percent yield based on starting ketone.

From Distilled Saturated Ester. Distilled hydroxy ester, 3.8 g., (prepared as previously described) was subjected to dehydrogenation over 1.0 g. of 10 percent palladium charcoal. The apparatus was flushed with nitrogen and the temperature increased slowly. At 240-250° a sudden violent evolution of water was observed, followed by the normal, smooth evolution of hydrogen at 310°. Heating was continued for another hour, during which time the temperature was raised gradually to 360°. A total volume of 400 ml. of hydrogen was evolved, a good deal of which (250 ml.) was obtained in the first five minutes. The theoretical quantity of hydrogen at this temperature and pressure (20°, 620 mm.) would be 380 ml.

The dehydrogenated material was extracted with ether, the solvent was removed, and the residue was saponified in a mixture of 80 ml. of methanol and 20 g. of potassium hydroxide by refluxing for ten hours. Excess methanol was removed, the residue was diluted with water, and non-saponifiable material was removed by ether extraction. The alkaline solution was cooled in an ice bath and acidified with 1:1 hydrochloric acid. A brown gum separated, that changed to a tan crystalline solid when allowed to stand. The material was filtered, washed and dried to give 2.3 g. of crude acid. The yield was 67 percent based on the hydroxy ester or 41 percent based on the starting ketone. Recrystallization of the material from benzene gave pure  $\gamma$ -(4-phenanthryl)butyric acid, melting 138-140° C. uncorr. compare Pachmann and Edgerton (4), 139.5-141° C. corr. . Analysis. Calculated for  $C_{18}H_{16}O_2$ : C, 81.8; H, 6.0. Found: C,       ; H       .

## Preparation of 4-Keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene

Two and one-half grams (.012 mole of phosphorus pentachloride was added to a solution of 2.3 g. (.0087 mole) of recrystallized  $\gamma$ -(4-phenanthryl)butyric acid in 15 ml. of anhydrous benzene. The mixture was allowed to stand for one hour with occasional swirling. After cooling in an ice bath, 2 ml. of anhydrous stannic chloride was added slowly, with swirling, to form a dark-red complex. After standing for 15 minutes the complex was decomposed with cold dilute hydrochloric acid. The organic layer was washed with dilute hydrochloric acid, with water, with 5 percent sodium bicarbonate, and finally with water. The solution was dried over anhydrous magnesium sulphate and the benzene removed to give the crude 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene as tan crystals, 2.0 g. (93 percent). The crude product was subjected to vacuum distillation to give 1.9 g. (89 percent) of pure colorless distillate. Recrystallization from acetone gave a product melting at 124.5-126° C. corr. . The 2,4-dinitrophenylhydrazone was prepared from this material and recrystallized from nitrobenzene. The orange product melted at 305-306° with decomposition. Analysis. Calculated for  $C_{18}H_{14}O$ : C, 87.8; H, 5.7. Found: C,       ; H,       .

In other experiments it was found that the crude  $\gamma$ -(4-phenanthryl)butyric acid, taken directly from the precipitation, was quite suitable for cyclization and gave yields comparable to that of the recrystallized acid.

## Preparation of 4-methylbenzo [c] phenanthrene

Clean magnesium turnings, 0.5 g., were introduced into a dry, 100 ml., round-bottom flask. A condenser was attached, 25 ml. of anhydrous ether was added, and about 5 ml. of a solution of 2.5 g. (.018 mole) of methyl iodide

in 25 ml. of anhydrous ether was run in to start the reaction. After warming on a hot water bath the reaction proceeded vigorously and the remainder of the methyl iodide solution was added dropwise through the condenser over a period of 10 minutes. The mixture was refluxed on a hot water bath for an additional 30 minutes until only a small amount of magnesium remained undissolved.

To the cold Grignard mixture was added dropwise with swirling over twenty minutes a solution of 0.95 g. (.0039 mole) of 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene in 30 ml. of 1:1 ether-benzene. A yellow insoluble complex formed, which however, dissolved to a greenish solution when the mixture was warmed. The solution was refluxed for 10 minutes, and was then poured into a mixture of ice and 10 percent sulfuric acid. The organic layer was again washed with cold 10 percent sulfuric acid and then with water until the washings were neutral to litmus. The organic layer was dried over anhydrous magnesium sulphate and the solvent was removed with a current of air. A white crystalline solid which remained melted at 122-125° C. This material, which was taken to be the crude tertiary carbinol, 4-methyl-4-hydroxy-1,2,3,4-tetrahydrobenzo [c] phenanthrene, could not be recrystallized from alcohol, alcohol-benzene or ether. In all cases complete removal of the solvent gave a viscous oil which formed no crystals upon cooling.

The crude carbinol (1.0 g.) was heated with 0.1 g. of 10 percent palladium charcoal in a nitrogen-flushed apparatus. Moisture was given off gradually between 250-300° and hydrogen evolution began at about 230°. The temperature was raised to 320-330° and kept there for one-half hour, until evolution of gas had ceased—a total of .023 mole of hydrogen being collected.

The product was extracted with benzene, dried over anhydrous magnesium sulphate and filtered. The removal of the solvent, followed by vacuum distillation of the residue gave 0.60 g. of a clear colorless oil. The picrate of 4-methylbenzo [c] phenanthrene, prepared from this material, crystallized as orange-red needles. Recrystallization of this material from alcohol-petroleum ether gave a product melting at 107-108.5°, uncorr. compare Hewett (14). 107-108°; and Newman, et. al. (20), 109.5-111.0°. The yield of picrate, 0.64 g. based on 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, was 35 percent. The over-all yield from 4-keto-1,2,3,4-tetrahydrophenanthrene was 13 percent.

Preparation of 4-(1,2,3,4-Tetrahydrobenzo [c]  
phenanthryl) acetic Acid

Ten grams of clean 40 mesh zinc was added to a solution of 1.5 g. (.006 mole) of 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene dissolved in 25 ml. of anhydrous benzene in a 500 ml., three-necked flask equipped with a condenser, mechanical stirrer, and dropping funnel. A solution of 2.75 g. (.018 mole) of methyl bromoacetate in 15 ml. of anhydrous benzene was run in and a crystal of iodine was added to the heated mixture. When the reaction began, as evidenced by a change in color of the mixture to a golden-yellow, stirring was started and four 1 to 2 g. portions of fresh zinc were added at half-hour intervals. The reaction mixture changed in color to an olive-brown and at the end of three hours formed a brown, insoluble complex.

At the end of the reaction period the complex was dissolved in 10 ml. of glacial acetic acid and poured into a slurry of ice and dilute hydrochloric acid. The flask was rinsed out with two-10 ml. portions of 1:1 acetic acid-

ether and the washings added to the main portion. The organic layer was washed with cold dilute hydrochloric acid, with water, and dried over anhydrous magnesium sulphate. A permanganate test on the dried solution gave a weakly positive test for unsaturation. Removal of solvent left a brown-oil residue amounting to 1.9 g.

This residue was dehydrated by heating with anhydrous formic acid in an oil bath at 95° for fifteen minutes. The oil, which was originally soluble in the formic acid, separated as an insoluble dark-brown gum during this heating period. The material was taken up in 25 ml. benzene and washed with water, 5 percent sodium bicarbonate, and again with water. The solution was dried, the solvent was removed and the residue dissolved in 30 ml. of 1:1 acetic acid-methanol (0.3g. of brown solid remained undissolved). Raney nickel catalyst (2 g.) was added and the mixture was hydrogenated at 40 psi for one hour. At the end of this time the material gave a negative unsaturation test. The catalyst was removed by filtration, 50 ml. of ether was added, and the solution was washed with water. The solvent was removed and the residue was saponified in a solution of 5 g. potassium hydroxide in 25 ml. methyl alcohol by refluxing for six hours. Excess methyl alcohol was removed, the residue was diluted with 50 ml. water, and nonsaponifiable material extracted with ether. The alkaline solution was cooled in an ice-bath, and acidified with 1:1 hydrochloric acid. A cream-colored acid precipitated, which was filtered, washed and dried. Crude 4-(1,2,3,4-tetrahydrobenzo [c] phenanthryl)acetic acid was obtained; 0.95 g., (54 percent). A sample, recrystallized from benzene, melted at 159-161° C. Analysis. Calculated for C H O : C, 82.8; H, 6.2. Found: C, ; H, .

Attempted Preparation of 1,2,3,3a,4,5-Hexahydrobenz  
[1] acephenanthrylen-5-one

A solution of 0.70 g. (.0024 mole) of 4-(1,2,3,4-tetrahydrobenzo [c] phenanthryl)acetic acid dissolved in 5 ml. of benzene was treated with 0.8 g. (.0038 mole) of phosphorus pentachloride. The mixture was allowed to stand for one hour, with occasional swirling, and then was cooled in an ice bath. Anhydrous stannic chloride, (0.8 ml), was added slowly, giving a red-brown complex. The complex was allowed to stand 20 minutes, and decomposed in a slurry of ice and dilute hydrochloric acid. The organic layer was washed with water and 5 percent sodium bicarbonate, dried, and the solvent was removed. Vacuum distillation of the residue gave 0.06 g. of clear, slightly yellowish distillate. Recrystallization of this distillate from benzene-acetone gave crystals melting at 161-164° C. This material was found to be soluble in 5 percent sodium bicarbonate solution, and gave no ketone test with 2,4-dinitrophenylhydrazine. It was therefore taken to be unreacted acid, and indicated that no cyclization had occurred.

#### DISCUSSION

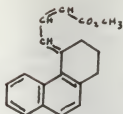
The synthetic route to 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene appears to be a decided improvement over the Bachmann-Edgerton synthesis previously cited. In addition to decreasing the length of the synthesis by two steps, a substantial increase in yield has been effected. The conversion from 4-keto-1,2,3,4-tetrahydrophenanthrene to 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene was carried out in 37 percent over-all yield, as compared to a 10 percent over-all yield obtained in the former synthesis. This route may also be favorably compared with the excellent

Diels-Alder synthesis, of the benzo c phenanthrene nucleus. If we consider the starting material (4-keto-tetrahydrophenanthrene) to be analogous to the starting material in the Diels-Alder synthesis (substituted  $\alpha$ -tetralones).

Methyl  $\gamma$ -methyl- $\gamma$ -bromocrotonate has been reported to be active in the Reformatsky reaction cf. Fuson and Southwick (11) and could undoubtedly be used to good advantage in this type of synthesis. By the use of this reagent it is highly probable that 1-methylbenzo [c] phenanthrene could also be prepared by the procedure presented here and quite possibly in yield as good as that for the 4-methyl derivative. It could also have been used to good advantage in the Newman and Hussey synthesis of 1,4,5-trimethylphenanthrene (Newman and Hussey, 17), where a double Arndt-Eistert reaction was used in a chain lengthening sequence. The key reaction of the synthesis in so far as difficulties were concerned, turned out to be the Reformatsky reaction between 4-keto-1,2,3,4-tetrahydrophenanthrene and methyl  $\gamma$ -bromocrotonate. This reaction was complicated by the tendency to form the diene ester, instead of the normal hydroxy ester, and was attended presumably by some polymerization of this diene in the reaction-mixture itself. This was evidenced by the production, during some reactions, of a red gummy material which clung to the walls of the flask and tended to hinder good agitation of the zinc. A similar type of material was observed in some early purification attempts, when the oily product from the reaction was subjected to vacuum distillation. No distillate was recovered (other than unreacted ketone) and a red, non-volatile viscous material remained in the distillation flask. Another indication of the presence of the diene was the golden-yellow color of the Reformatsky product. This color was lost completely on hydrogenation. Such behavior would be expected of the conjugation present in the



diene ester.



The production of the diene ester would not be objectionable if it remained stable throughout the reaction, and could subsequently be hydrogenated to the saturated ester. However, as noted, its presence tends to give rise to gummy material, which in turn leads to a decided decrease in yield further along in the synthesis. This is explained a little later. It has been suggested that this material arises as a result of a Diels-Alder addition between the diene ester and the hydroxy ester, both of which are undoubtedly present to some extent in any given reaction mixture. While there is some plausibility in this explanation it is far more likely that simple polymerization may be the cause of this loss of material. In support of this it may be noted that in all other cases of reactions between methyl  $\gamma$ -bromocrotonate and cyclic ketones no difficulty of this sort was reported, even where the diene ester was known to be the main product of the reaction. The difference must lie in the fact that, without exception, these were all carried out on ketones in which there was no aromatic ring adjacent to the carbonyl group and thus no opportunity for such conjugation as we have in the present case. Besides being a driving force for the loss of water from the hydroxy ester, this conjugation must also be responsible for the greater ease of polymerization which was observed.

In connection with this discussion of the diene ester a logical explanation may be offered for the failure of the attempted conversion of the

crude Reformatsky product directly to methyl  $\gamma$ -(4-phenanthryl)butyrate. It was found in the case of the saturated hydroxy ester that water was lost at a temperature (240-250°), well below that required for the removal of hydrogen. If this occurred with the unsaturated hydroxy ester we would have the diene ester produced at a temperature considerably above that at which polymerization is known to occur, and the obvious result would follow. This would explain the production of a large amount of tarry material and little recoverable acid.

Fortunately for the synthesis, it was found that the hydroxy ester could be isolated as the major product of the reaction if the reflux period and amount of solvent were carefully controlled. If, the reflux period is not carried beyond three to four hours and a goodly quantity of benzene is used as solvent yields of over 60 percent of hydroxy ester can be obtained. Proof that the hydroxy ester was indeed the product was obtained by a series of experiments on the ester obtained by hydrogenating the Reformatsky product. Upon vacuum distillation this ester was obtained as a clear colorless oil, which was originally assumed to be the saturated ester, methyl  $\gamma$ -[4-(1,2,3,4-tetrahydrophenanthryl)]crotonate. However, upon treatment of this distillate with palladium-charcoal it was found to split out water at 240-250°, followed at 320-330° by the evolution of a little over one-half of the theoretical amount of hydrogen which could be expected for methyl  $\gamma$ -[4-(1,2,3,4-tetrahydrophenanthryl)]crotonate. This clearly indicated hydroxy ester. Indirect confirmation was given by two additional experiments. In one the hydrogenated Reformatsky product was dehydrogenated directly with palladium charcoal to give (after saponification) a 35 percent yield of  $\gamma$ -(4-phenanthryl)butyric acid. However, when the hydrogenated Reformatsky product was saponified, re-esterified and the resultant ester dehydrogenated, only a 16 percent yield

of the same acid was obtained. This marked decrease in yield was more than could be explained by losses during the purification procedure and must have been caused by cleavage of the hydroxy ester during saponification. This type of cleavage is a well-known property of such hydroxy esters, and has been reported in a number of cases (1, 21). Alkaline cleavage was also observed to occur with the unsaturated Reformatsky product, and in this case the 4-keto-1,2,3,4-tetrahydrophenanthrene produced was isolated and identified.

As stated above it is possible to convert the crude saturated Reformatsky ester directly, without purification to  $\gamma$ -(4-phenanthryl)butyric acid. The yield is comparable to that obtained from the distilled product. The acid obtained is not quite as pure as that obtained from the distilled ester, but this does not matter if the material is to be carried on to 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene since it was found that cyclization occurs as readily and in as good yield with the crude acid as with material of higher purity. Since unreacted ketone is not removed when dehydrogenation is carried out directly it will be converted, in part, into 4-phenanthrol cf. Mosettig and Duvall (16) and be carried into the alkaline fraction after saponification of the dehydrogenated product. This impurity can be readily removed however by precipitation of all acidic material, re-solution in sodium bicarbonate, and extraction of the 4-phenanthrol with ether.

The combined dehydration-dehydrogenation of the distilled hydroxy ester was accomplished in lower yield (67 percent) than expected. This was most likely due to a reductive cleavage at the point of chain attachment. Such a reductive cleavage has been reported by Newman and Wheatley (18) for the palladium-charcoal catalyzed dehydration-dehydrogenation of methyl  $\alpha$ -[4-(4-hydroxy-1,2,3,4-tetrahydrophenanthryl)] propionate. After hydrolysis a

10.5 percent yield of phenanthrene was recovered in the neutral fraction, indicating partial scission of the side chain.

The importance of solvent in the Reformatsky reaction was discovered in a rather unfortunate reaction which was run after the route to  $\gamma$ -(4-phenanthryl)butyric acid had been worked out. In order to prepare a workable quantity of 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, a somewhat larger Reformatsky condensation was carried out using 0.1 mole of ketone. Conditions were exactly the same as used previously, with the exception that one-half the amount of benzene was employed. The usual thick yellow complex was formed, and to all appearances the reaction was going smoothly. However, after one hour of refluxing an abnormal amount of reddish gum was observed to be collecting on the walls of the flask. This tended to cement the zinc granules and efficient agitation was made difficult. The reaction mixture was worked up in the usual manner, the residue hydrogenated and vacuum distilled. Distillation took place with difficulty and considerable brownish material was carried over into the distillate. Dehydrogenation and saponification gave only a 15 percent yield of acid, which was dark and quite impure. This reaction sequence is cited as an example of the complications which follow if the Reformatsky reaction is not carefully controlled, and diene ester is allowed to form.

The effect of decreasing the amount of solvent is, of course, actually one of temperature, since this allows a higher concentration of dissolved complex and a resulting increase in the reflux temperature. Water is then more easily split out of the hydroxy ester, diene ester is formed and polymerization occurs. The same sequence of events undoubtedly occurs if the reflux period is prolonged. Bachmann, and Wendler (6) have avoided the

formation of diene ester by use of a mixture of ether and benzene—presumably to lower the reflux temperature. However, in the present case the higher reflux temperature of benzene alone was found necessary to activate the reaction, which at best is rather difficult to start. It might prove worthwhile to start the reaction with pure benzene, and then, to add ether when the reaction is well under way.

The remainder of the synthetic work was straight-forward and needs little comment. Cyclization of  $\gamma$ -(4-phenanthryl)butyric acid proceeded readily and in high yield. The yield of saturated acid from the Reformatsky condensation of methyl bromacetate with 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene was a bit low, but comparable with yields obtained with certain other four-ring ketones (10). Cyclization of 4-(1,2,3,4-tetrahydrobenzo [c] phenanthryl) acetic acid failed to take place. However, there is no reason to suppose that such a cyclization will not be successful, providing a suitable procedure can be found. A higher reaction temperature, or use of a different catalyst, such as aluminum chloride or hydrofluoric acid, may be the key to this cyclization. Lack of time did not permit further experiments and the final conversion to benz [1] acephenanthrylene. Once prepared, this hydrocarbon may be of interest as a possible carcinogen.

#### SUMMARY

4-Keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene has been synthesized by a new route involving a Reformatsky condensation between methyl  $\gamma$ -bromocrotonate and 4-keto-1,2,3,4-tetrahydrophenanthrene. The hydroxy ester produced by this reaction was hydrogenated, dehydrated, dehydrogenated and hydrolyzed to give  $\gamma$ -(4-phenanthryl)butyric acid. Cyclization of this acid gave the desired ketone in 37 percent over-all yield.

Indirect evidence has been given for the production to some extent, of diene ester in the Reformatsky reaction. Depending on the conditions of the reaction, polymeric material attributable to this ester may arise resulting in impure product and lower yields. Both the unsaturated and saturated hydroxy esters from the Reformatsky reaction were found to undergo alkaline cleavage.

4-Methylbenzo [c] phenanthrene was prepared by means of a Grignard reaction with 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene and methyl iodide, followed by dehydration-dehydrogenation of the resultant carbinol to the hydrocarbon. The over-all yield from the starting material is comparable to that obtained by previous syntheses of this hydrocarbon.

4-(1,2,3,4-Benzo [c] phenanthryl)acetic acid was prepared by a Reformatsky reaction between 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene and methyl bromoacetate. Dehydration, hydrogenation and hydrolysis of the ester so produced gave the desired acid in 54 percent yield. This acid has not been reported previously. An attempted cyclization of this acid to 1,2,3,3a,4,5-hexahydrobenz [1] -acephenanthrylene-5-one failed.

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SYNTHESIS OF BENZO [C] PHENANTHRENE  
AND RELATED COMPOUNDS

by

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B. S., Kansas State College  
of Agriculture and Applied Science, 1950

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AN ABSTRACT OF A THESIS

submitted in partial fulfillment of

requirements for the degree

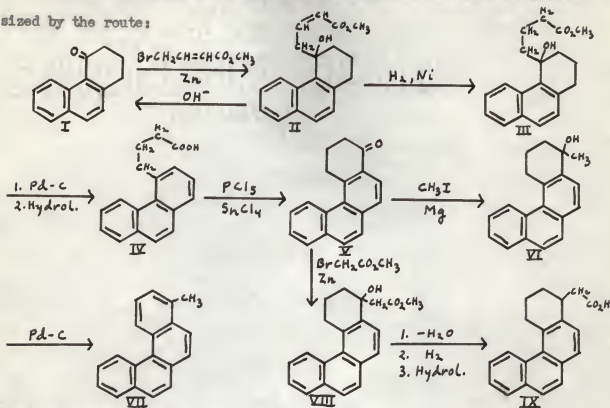
MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE  
OF AGRICULTURE AND APPLIED SCIENCE

1955

Compounds containing the benzo [c] phenanthrene nucleus were synthesized by the route:



The starting material, 4-keto-1,2,3,4-tetrahydrophenanthrene, (I), was prepared from naphthalene by succinylation to produce  $\beta$ -naphthoylpropionic acid, followed by reduction of this acid to  $\beta$ -naphthylbutyric acid and cyclization. A Reformatsky reaction with methyl  $\gamma$ -bromocrotonate gave methyl  $\gamma$ -[4-(4-hydroxy-1,2,3,4-tetrahydrophenanthryl)] crotonate, (II), as a reddish-yellow oil which polymerized on heating at  $200^\circ$  and underwent alkaline cleavage to give the original ketone (I). Reduction of II gave methyl  $\gamma$ -[4-(4-hydroxy-1,2,3,4-tetrahydrophenanthryl)] butyrate, (III), as a colorless, viscous oil, in 62 percent yield based on I. Indirect evidence indicated that this ester also undergoes alkaline cleavage. Treatment of III, with 10 percent palladium charcoal, followed by saponification, gave  $\gamma$ -(4-phenanthryl)butyric acid, (IV), in 67 percent yield; mp.  $138-140^\circ$ . An attempt to convert II directly to the methyl ester of  $\gamma$ -(4-phenanthryl)-butyric acid by treating with palladium-charcoal resulted in failure.

Cyclization of IV proceeded readily to give 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, (V), in 89 percent yield; mp. 124.5-126°. A 2,4-dinitrophenylhydrazones prepared from V melted at 305-306°, (decomp.).

Two condensation reactions were carried out on 4-keto-1,2,3,4-tetrahydrobenzo [c] phenanthrene, (V). A Grignard reaction between V and methyl iodide gave the tertiary carbinol, 4-methyl-4-hydroxy-1,2,3,4-tetrahydrobenzo [c] phenanthrene, (VI) as a crystalline solid; mp. crude product 122-125°. Treatment of the crude carbinol with 10 percent palladium-charcoal produced 4-methylbenzo [c] phenanthrene, isolated as the picrate in 35 percent yield from V. The recrystallized picrate melted at 107-108.5°. In the second conversion a Reformatsky reaction between V and methyl bromoacetate gave the hydroxy ester (VIII). The crude ester was dehydrated with anhydrous formic acid, hydrogenated, and saponified to give 4-(1,2,3,4-tetrahydrobenzo [c] phenanthryl) acetic acid, (IX), mp. 159-161°. Treatment of IX with phosphorus pentachloride and anhydrous stannic chloride failed to effect cyclization to produce 1,2,3,3a,4,5-hexahydrobenz [1] acephenanthrylene.

