ment with petroleum ether to remove unchanged cyclohexylresorcinol and three crystallizations from carbon tetrachloride there was obtained 0.71 g. of product, m. p. 145°. The yield was 15%.

Anal.[12] Calcd. for $C_{12}H_{10}O_2$: C, 77.41; H, 5.41. Found: C, 77.19; H, 5.65.

Summary

1. The action of potassium benzoate upon 3,5- and 2,4-dibromobiphenyls gives monohydroxybiphenyl benzoates, one bromine being replaced by hydrogen.

2. 4-Phenylresorcinol and the 5-isomer have been synthesized by dehydrogenation reactions.

3. These resorcinol derivatives have but little activity as bactericidal agents.

EVANSTON, ILLINOIS RECEIVED NOVEMBER 21, 1938

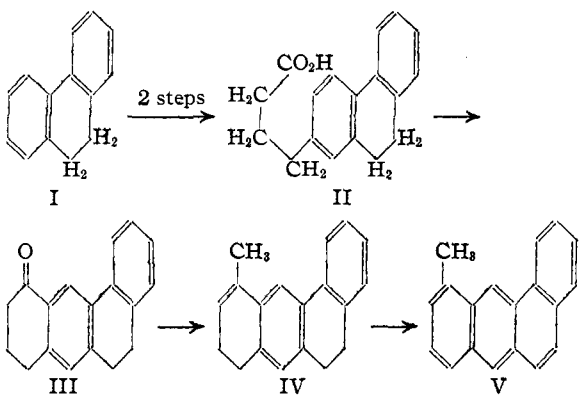
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

8-Methyl-1,2-benzanthracene

BY LOUIS F. FIESER AND WILLIAM S. JOHNSON[1]

While one of two hydrocarbons recently described by Cook and Robinson[2] corresponds well in properties with the sample of 1′-methyl-1,2-benzanthracene previously synthesized in this Laboratory,[3] the substance which they regard as 8-methyl-1,2-benzanthracene differs considerably from a hydrocarbon believed to have this structure which we had synthesized at the time of the appearance of their paper. After repeating the preparation with the same results and investigating the purity and identity of the intermediates, we are now placing our observations on record.

The starting material, 9,10-dihydrophenanthrene, was prepared according to Burger and Mosettig[4] and Durland and Adkins[5] by hydrogenation of phenanthrene over copper chromite catalyst. By conducting the reaction at 160° without solvent and avoiding the formation of the difficultly separated *s*-octahydride, it was found possible to obtain material of excellent purity (m. p. 32–33°) after a single fractionation at 7–8 mm. from unchanged phenanthrene. Condensation of this material with succinic anhydride in the Friedel and Crafts reaction gave the β-(9,10-dihydro-2-phenanthroyl)-propionic acid of Burger and Mosettig[6] in a satisfactory condition in 96% yield. This was reduced to II as described by these authors, but since they had found cyclization with 85% sulfuric acid to give a low yield (30%) of the ketone III, other methods were investigated. Ring closure with zinc chloride in



acetic acid–anhydride solution nearly doubled the yield, but it was found still more satisfactory to treat the acid in benzene with phosphorus pentachloride, followed by aluminum chloride.

The 8-keto-3,4,5,6,7,8-hexahydro-1,2-benzanthracene (III) obtained easily by this method in 63% yield (pure) was found to exist in two polymorphic forms of different melting point, one of which corresponded to the sole product encountered by Burger and Mosettig, who established the structure of their substance by conversion to 1,2-benzanthracene. It seemed desirable to eliminate any doubt about the direction of ring closure under the conditions employed in the present work, and consequently a sample obtained with the use of phosphorus and aluminum chlorides was reduced and dehydrogenated. The sole product was 1,2-benzanthracene. It was also found that both crystalline modifications can be obtained from ketone prepared by cyclization with sulfuric acid and that the two forms

(1) Holder of the John Woodruff Simpson Fellowship from Amherst College.

(2) J. W. Cook and Mrs. A. M. Robinson, *J. Chem. Soc.*, 505 (1938).

(3) Fieser and Seligman, THIS JOURNAL, **60**, 170 (1938).

(4) Burger and Mosettig, *ibid.*, **58**, 1857 (1936).

(5) (a) Durland and Adkins, *ibid.*, **59**, 135 (1937); (b) **60**, 1501 (1938).

(6) Burger and Mosettig, *ibid.*, **59**, 1302 (1937),

are interconvertible. The product of cyclization by either method therefore has the structure III and the material used in the present synthesis, since it was carefully purified through the semicarbazone, is not likely to have contained any appreciable amount of the isomeric ketohexahydrochrysene.

Dehydration of the carbinol resulting from the reaction of III with methylmagnesium chloride gave a nicely crystalline tetrahydride, presumably of the structure IV. Like simpler benzenoid hydrocarbons having a conjugated double bond in the side chain, the substance forms a picrate. Dehydrogenation with either sulfur or selenium gave a hydrocarbon having the composition of the expected 8-methyl-1,2-benzanthracene and giving a 1,2-benzanthraquinone (vat test) on oxidation. The hydrocarbon exists in two forms and shows a double melting point, and the homogeneity was checked by purification through the bright red picrate, by chromatographic adsorption, crystallization, and sublimation. A comparison of the melting points of our samples with those of Cook and Robinson is given in the table and it is evident that there is considerable divergence, particularly in the melting point characteristics for the hydrocarbon itself. Since the eleven other methyl-1,2-benzanthracenes all melt at higher temperatures (125 to 194°), confusion with another isomer does not seem likely, and it would appear that the lower melting sample is impure.

COMPARISON OF PROPERTIES

	Cook and Robinson, m. p., °C.	Present work, m. p. °C. (corr.)
Hydrocarbon	107	113.5–114, 118–118.5
Picrate	161–162	159.5–160
Trinitrobenzene derivative	164–165	169.5–170
Quinone	191–192	196.5–197

Experimental Part[7]

9,10-Dihydrophenanthrene.—Phenanthrene from the Gesellschaft für Teerverwertung was found to be contaminated with considerable sulfur-containing materials which completely inhibited hydrogenation. It was therefore stirred vigorously (Hershberg stirrer) at 200° (sand-bath) with 10% of sodium for six hours, as described by Durland and Adkins;[5a] the hydrocarbon was extracted from the cooled mass by prolonged refluxing with benzene and the cooled solution was filtered cautiously from the black residue, which was allowed to decompose (with ignition) out of doors. The sulfur-free phenanthrene obtained on distillation amounted to 72.5% of the starting material.

Hydrogenation in the presence of copper chromite catalyst 37 KAF was tried under various conditions recommended,[4,5] and a solvent was soon dispensed with as unnecessary. In conformity with the observations of Durland and Adkins,[5] we found that at 220°, the temperature employed by Burger and Mosettig,[4] an appreciable amount of the *s*-octahydride invariably was formed and could not subsequently be removed effectively from the dihydride by fractionation. The best results were obtained at 160°, but even at this temperature it seemed advisable to sacrifice yield for purity by stopping the reaction somewhat short of the point at which the phenanthrene was all consumed and thus avoiding the formation of difficultly separated higher hydrides. Contrary to the experience of Durland and Adkins,[5b] no difficulty was encountered in separating the 9,10-dihydride from phenanthrene by distillation at 7–8 mm.

In a typical experiment 267.1 g. of pure phenanthrene was mixed with 10% of catalyst and hydrogenated at 3000 lb. (200 atm.) initial pressure at 160° until the gas absorption was approximately 90% of the theoretical. The extracted product on fractionation through a 1-meter column packed with glass helices yielded 180 g. of 9,10-dihydrophenanthrene, b. p. 154.0° at 7.5 mm., m. p. 32–33°, $n^{25}D$ 1.6418–1.6431. For chemically purified and recrystallized material, Schroeter, Müller and Huang[8] give the m. p. 34.5–35°. The higher boiling residue can be combined with fresh phenanthrene in a second hydrogenation.

β-(9,10-Dihydro-2-phenanthroyl)-propionic acid was prepared from the above sample of hydrocarbon (139 g.) as described by Burger and Mosettig[6] except that the aluminum chloride was added gradually to a stirred mixture of the other components at 0°. The crude acid precipitated from a soda solution was suitable for reduction; m. p. 154–156° (once crystallized, 157–158°); yield, 207 g. (96%).

The only change in the procedure[6] for the preparation of γ-(9,10-dihydro-2-phenanthryl)-butyric acid consisted in using more toluene (100 cc. for 50 g. of keto acid); the product, purified by vacuum distillation, was obtained as reported[6] in 85% yield (crystallized from benzene–ligroin, m. p. 92–92.5°).

8-Keto-3,4,5,6,7,8-hexahydro-1,2-benzanthracene.—One crystalline modification of this ketone separates from ligroin, methanol, or acetic acid in the form of colorless blades, m. p, 92°, The other, which is the modification described by Burger and Mosettig,[6] crystallizes from the same solvents as lustrous prisms, m. p. 97–98°. The low-melting form on being warmed in an oven at 60° is slowly transformed into the prism form, and after several hours only the higher melting point is observed. When heated at the usual rate in a capillary tube the blade form melts at 92°, and the material which solidifies on cooling remelts at about 97° or, if the process is repeated, sharply at 97–98°. Either modification can be caused to crystallize from the solutions or the melt by appropriate seeding, and the crystals separating from solution are usually either all prisms or all blades, The substance is thus most

(7) All melting points are corrected.

(8) Schroeter, Müller and Huang, *Ber.*, **62**, 645 (1929).

fully characterized by observing the two crystalline forms and the double melting point, as indicated briefly in the following notations.

(a) *With Zinc Chloride.*—The best results were obtained when the amount of catalyst was increased considerably beyond that originally specified for acetylative cyclization.[9] A mixture of 6.25 g. of the dihydrophenanthrylbutyric acid (II), 3.2 g. of zinc chloride, 18 cc. of glacial acetic acid, and 12 cc. of acetic anhydride was refluxed for one hour. Water was added cautiously by drops under reflux to decompose the anhydride, and the cooled mixture was diluted and extracted with ether. Extraction with ammonia removed a small amount of acid, and after drying with potassium carbonate the product was distilled in vacuum, giving 3.45 g. (59%) of crude ketone. Two crystallizations from benzene–ligroin gave the blade form melting at 90.5–91.5° and remelting at 96–97°. In comparison with the derivatives described by Burger and Mosettig,[6] the semicarbazone formed shiny plates from acetic acid, decomposing indefinitely above 250°, and the oxime crystallized from alcohol as prisms, m. p. 199–201°, dec. A sample of the ketone regenerated from the semicarbazone by boiling for twenty minutes with 6 *N* hydrochloric acid formed blades, m. p. 92°; after solidification, m. p. 97–98°.

(b) *Through the Acid Chloride.*—A mixture of 40 g. of the acid II and 36.2 g. of phosphorus pentachloride in 350 cc. of dry benzene was heated gradually with stirring and then refluxed for one hour. After cooling in ice, 36.2 g. of aluminum chloride was added with stirring, and after standing for several hours without external cooling the mixture was refluxed for one and one-half hours. After treatment with ice and acid and steam distillation the product was washed in ether with soda solution, which removed 4.2 g. of somewhat impure starting material. On vacuum distillation there was obtained 30.8 g. of crude ketone (82.5%, not allowing for recovered acid).

A 10-g. sample of this crude ketone was converted to the semicarbazone, which was obtained after one crystallization from glacial acetic acid in a pure condition; yield, 11.4 g. (90.5%). This was hydrolyzed and the ketone distilled and crystallized from ligroin, giving 5.6 g., m. p. 90–91, and 96–97° (56% recovery from crude product).

Material of equal purity, as judged by melting points, was obtained by one crystallization of the crude ketone from ligroin, distillation (2 mm., colorless distillate), and crystallization from ligroin, the recovery being 77%.

For purposes of identification a sample of the semicarbazone (0.7 g.) was heated with sodium ethylate (Burger and Mosettig[6]), the oil dehydrogenated with sulfur, and the product distilled and crystallized repeatedly from alcohol. This gave fluorescent, but somewhat yellow, material, m. p. 159–160°, giving no depression when mixed with authentic 1,2-benzanthracene (colorless, m. p. 160–160.5°).

(c) *With Sulfuric Acid.*—Cyclization of the acid II with 85% sulfuric acid proceeded as described by Burger and Mosettig.[6] By suitable seeding, the product was obtained in both the blade and prism form having the melting point characteristics described above and giving no depression when mixed with the other samples. The semicarbazone also had the same properties as before.

(9) Fieser and Hershberg, THIS JOURNAL, **59**, 1028 (1937).

8-Methyl-3,4,5,6-tetrahydro-1,2-benzanthracene (IV).—An ethereal solution of 6 g. of the ketone was added with stirring to a chilled Grignard solution from 1.5 g. of magnesium and excess methyl chloride. After refluxing for five hours, the complex was decomposed with acid and the material extracted with ether, washed, and dried. After removal of the solvent, the product was heated at 130–160° at 1 mm. for four hours to effect dehydration and distilled, b. p. about 175° (1 mm.), giving a highly fluorescent, colorless oil which solidified on standing; yield, 5.1 g. (86%); m. p. 50–55°. A sample crystallized three times from methanol formed colorless, elongated plates, m. p. 70–70.5°. The picrate forms scarlet needles from alcohol, m. p. 140–141°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.63; H, 7.37. Found: C, 92.62; H, 7.29.

8-Methyl-1,2-benzanthracene.—In one experiment 3.27 g. of the tetrahydride IV purified merely by distillation (m. p. 50–55°) was heated with 0.85 g. of sulfur at 230–240° until hydrogen sulfide was no longer evolved (forty-five minutes) and the product distilled at 1 mm. from a small amount of zinc dust. The resulting yellow solid was taken into benzene and the solution clarified by filtration through a tower of activated alumina. The process was repeated, the solvent removed, and the hydrocarbon converted into the picrate in alcoholic solution. One recrystallization from alcohol gave 3.53 g. (56%) of satisfactory picrate, m. p. 158–159°. Further purified for analysis, the substance formed flat, deep red needles, m. p. 159.5–160°.

Anal. Calcd. for $C_{19}H_{14}\cdot C_6H_3O_7N_3$: N, 8.91. Found: N, 9.10.

A portion of the picrate (0.5 g.) was cleaved by passing a benzene solution through a tower of alumina, and the colorless product recovered from the filtrate was crystallized twice from alcohol (0.14 g.). The hydrocarbon separated from this solvent in a completely colorless condition in the form of either plates or needles of the same melting point. The substance melts sharply at 118–118.5°, but after the material has been allowed to solidify and is remelted several times it changes to another modification melting at 113.5–114°. Distillation or sublimation gives mixtures of intermediate melting point, but crystallization from alcohol invariably produces the higher melting modification. Thus the sample for analysis was sublimed and crystallized, giving needles, m. p. 118–118.5°, remelting at 113.5–114°.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.35; H, 5.71.

The **trinitrobenzene derivative** formed bright orange needles from alcohol, and the sample after two recrystallizations melted at 169.5–170°.

The hydrocarbon was also prepared by dehydrogenating 1 g. of the pure tetrahydride IV (m. p. 70–70.5°) with selenium at 300°. The product was extracted with benzene, the solution clarified with an adsorption tower, and the product crystallized from alcohol, giving 0.53 g. of hydrocarbon, m. p. 112–116°. This was purified through the picrate, yielding 0.8 g. of recrystallized material, m. p. 158–159°, and the hydrocarbon recovered from the complex (0.5 g.) as above and twice recrystallized from alcohol formed almost colorless plates (0.15 g.), m. p.

116.5–118° and 112.5–113°, giving no depression when mixed with the above product of sulfur dehydrogenation.

8-Methyl-1,2-benzanthraquinone was prepared by refluxing the pure hydrocarbon (0.4 g.) in glacial acetic acid (8 cc.) for eighteen minutes with potassium dichromate (0.49 g.) and diluting the solution with water. The crude quinone which crystallized was dried, dissolved in benzene, and put through a tower of alumina. The chromatogram was developed with benzene and the bright yellow zone was separated and eluted with acetone in a Soxhlet extractor. The yellow crystallizate obtained after concentration when crystallized once from acetone formed bright yellow needles, m. p. 196.5–197° (0.11 g.). Two more crystallizations from acetone and one from benzene–ligroin did not raise the melting point. The quinone gives a blood red vat with alkaline hydrosulfite.

Anal. Calcd. for $C_{19}H_{12}O_2$: C, 83.81; H, 4.44. Found: C, 84.15, 83.87;[10] H, 4.57, 4.56.[10]

(10) Analysis by the Arlington Laboratories.

8-Methyl-1,2-benzanthrahydroquinone diacetate, prepared by reductive acetylation in nearly quantitative yield and crystallized from acetic acid and from benzene–ligroin, formed colorless, felted needles, m. p. 202.5–203°.

Anal. Calcd. for $C_{23}H_{18}O_4$: C, 77.08; H, 5.06. Found:[10] C, 77.05; H, 5.24.

Summary

A hydrocarbon regarded as8 -methyl-1,2-benzanthracene has been synthesized from 9,10-dihydrophenanthrene through the known 8-keto-3,4,5,6,7,8-hexahydro-1,2-benzanthracene of Burger and Mosettig. The hydrocarbon has a double melting point and both modifications melt considerably higher than the substance described by Cook and Robinson.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

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[CONTRIBUTION FROM THE ANIMAL CHEMISTRY AND NUTRITION SUBSECTION OF IOWA STATE COLLEGE]

The Preparation of 3,5- and 4,6-Cholestadienes and a Study of Cholesterilene and of "7-Dehydrocholestene Isomer"[1]

BY J. C. ECK, RALPH L. VAN PEURSEM[2] AND E. W. HOLLINGSWORTH

In connection with our research on the chemical antirachitic activation of sterols,[3] an investigation was made concerning the preparation of 3,5- and 4,6-cholestadienes. A study also was made of cholesterilene and of the hydrocarbon, $C_{27}H_{44}$, obtained by Dimroth and Trautmann[4] by the vacuum distillation of the benzoate of 7-hydroxycholestene at a higher temperature or under a less evacuated condition than is necessary for the preparation of 7-dehydrocholestene and also by the action of acetic anhydride on 7-hydroxycholestene. This hydrocarbon, the structure of which has not been determined, has been referred to as the "isomeric hydrocarbon" by Stavely and Bergmann[5] and as the "cholestadiene, m. p. 91°, prepared by Dimroth and Trautmann" by Heilbron, Shaw and Spring.[6] For the sake of clarity in distinguishing this hydrocarbon from other cholestadienes, it will be referred to simply as "7-dehydrocholestene isomer" so as to avoid any possible confusion.

The preparation of 3,5-cholestadiene, m. p. 78–79°, $(\alpha)^{21}D$ −63.75, by means of a Wolf–Kishner reduction of 7-ketocholesterilene has been reported[7] but a more convenient method of preparation was desired. This was accomplished by the removal of two molecules of hydrogen bromide from pseudo-cholestene dibromide (4,5-dibromocholestane) by the action of quinoline. 4,6-Cholestadiene was likewise prepared from β-cholestene dibromide (5,6-dibromocholestane); α-cholestene dibromide also was used with equal success but the bromination product of cholestene consists chiefly of the β-isomer.

A halogen in the 5-position can be removed easily as hydrogen halide with a hydrogen atom from either the 4- or 6-position since alcoholic potassium acetate has been found to convert cholestene hydrochloride (5-chlorocholestane) to pseudo-cholestene[8] and to convert cholesterol hydrochloride (5-chlorocholestanol-3) to a mixture of cholesterol and allocholesterol.[9] It would be expected in the case of a dibromide of cholestane with one bromine atom in the 5-position and the other bromine atom in either the

(1) Journal Paper No. J579 of the Iowa Agricultural Experiment Station, Project No. 506.

(2) Part of the experimental work included in this paper is from unpublished research conducted by Ralph L. Van Peursem as partial fulfilment for the degree of Doctor of Philosophy.

(3) Eck, Thomas and Yoder, *J. Biol. Chem.*, **117**, 655 (1937); Eck and Thomas, *ibid.*, **119**, 621, 631 (1937).

(4) Dimroth and Trautmann, *Ber.*, **69B**, 669 (1936).

(5) Stavely and Bergmann, *J. Org. Chem.*, **1**, 575 (1937).

(6) Heilbron, Shaw and Spring, *Rec. trav. chim.*, **57**, 529 (1938).

(7) Stavely and Bergmann, *J. Org. Chem.*, **1**, 567 (1937).

(8) Mauthner and Suida, *Monatsh.*, **28**, 1113 (1907).

(9) Schoenheimer and Evans, *J. Biol. Chem.*, **114**, 567 (1936).