

concentrated hydrochloric acid and a trace of stannous chloride, boiled for three minutes, and diluted with three volumes of water. A microcrystalline product separated on cooling and this was collected by ether extraction and crystallized from ether-petroleum ether. Small colorless prismatic needles were obtained (29 mg.), and two recrystallizations brought the melting point to 154–154.8° (16 mg.).

Anal. Calcd. for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.30; H, 7.55.

(b) From the Ethyl Ester.—The ester of X (603 mg.), prepared as described below, was dissolved in 10 cc. of 30% potassium hydroxide containing 0.2–0.3 g. of sodium hydrosulfite in a flask flushed with nitrogen. The solution was refluxed under a slight pressure of nitrogen for one hour, the vat liquor remaining clear yellow. The solution was cooled slightly, acidified cautiously under nitrogen with 5 cc. of acetic acid, diluted with water and allowed to cool. The solid which separated was not easily filtered and was therefore extracted with ether. The extract was washed with saturated salt solution, concentrated and diluted with petroleum ether. On crystallization under forcing conditions, 504 mg. (92%) of colorless prismatic needles was obtained, m. p. 150–152° (after drying at 60° and 30 mm. to remove traces of acetic acid).

Ethyl ϵ -(5,8-Dihydro-1,4-naphthohydroquinonyl-2)-caproate.—A solution of 653 mg. of the diene addition product in 4 cc. of warm 95% ethyl alcohol was treated with 0.5 cc. of concentrated hydrochloric acid and a crystal of stannous chloride and heated for twenty-five minutes on the steam-bath. The ester did not crystallize readily on cooling but after some manipulation it formed rosetts of colorless needles. Collected, washed with acidified water, and dried in vacuum, the substance melted at 93–95.5° and depressed the melting point of the starting material; yield 633 mg. (88%). A sample crystallized twice from ether-petroleum ether melted at 95–96°.

Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.02; H, 7.95. Found: C, 70.67; H, 8.10.

ϵ -(1,4-Naphthoquinonyl-2)-caproic Acid (XI, $n = 5$).—To a pasty suspension of 504 mg. of ϵ -(5,8-dihydro-1,4-

naphthohydroquinonyl-2)-caproic acid in 4 cc. of acetic acid, a solution of 0.50 g. of chromic anhydride in 0.6 cc. of water and 1.5 cc. of acetic acid was added by drops. The material largely dissolved and a brown intermediate then separated and later dissolved. After warming at 60° for one-half hour, the solution was poured onto ice and the precipitate was collected and washed with water. The light yellow solid, which is but sparingly soluble in ether, crystallized from dilute methanol in centimeter-long needles of dull appearance melting at 142–146° (356 mg.). Two recrystallizations gave 300 mg. (60.5%) of product, m. p. 145.5–146.5°, but the dull appearance persisted. Recrystallization from benzene-hexane (Norit) gave 279 mg., m. p. 146.2–147.2°, and on a further crystallization from benzene the quinone formed fairly bright yellow leaf-like blades, m. p. 146–147.5° with slight preliminary softening. In the Craven test the substance gave a light lavender blue color deepening to a beautiful blue with a trace of purple.

*Anal.*¹³ Calcd. for $C_{16}H_{16}O_4$: C, 70.57; H, 5.92. Found: C, 70.56; H, 6.20.

Summary

Certain considerations suggest that, in the series embracing quinones having a fatty acid side chain, compounds may be found possessing interesting biological actions. As a first step in a study of such substances, the known *o*-hydroxybenzoyl derivatives of propionic and valeric acid were reduced by the Clemmensen method and the products were converted through the *p*-sulfo-benzeneazo and amino derivatives into γ -quinonylbutyric acid and ϵ -quinonylcaproic acid. These benzoquinones were converted, by the addition of butadiene, isomerization and oxidation, into the corresponding naphthoquinone acids.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

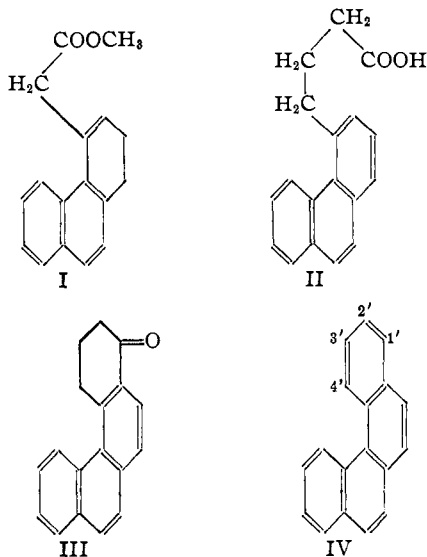
The Synthesis of 3,4-Benzphenanthrene and 1-Methylpyrene

BY W. E. BACHMANN AND R. O. EDGERTON¹

As starting material for the synthesis of the carcinogenic hydrocarbon 3,4-benzphenanthrene (IV) and of 1-methylpyrene (VIII) we employed the readily available 4-keto-1,2,3,4-tetrahydrophenanthrene. In the synthesis of the first hydrocarbon, the cyclic ketone was treated with zinc and methyl bromoacetate and the product of the Reformatsky reaction was dehydrated to methyl 4-(1,2-dihydrophenanthryl)-acetate (I). The ester group of this compound was reduced to

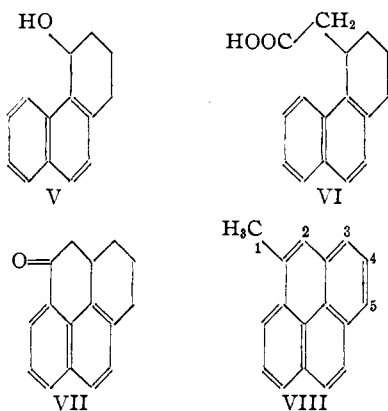
an alcohol group by sodium and methanol, the nucleus being reduced partially at the same time. The alcohol was converted to the corresponding bromide, which was condensed with sodio-malonic ester. The methyl ester of the acid obtained by decarboxylation of the substituted malonic acid was dehydrogenated to the ester of γ -(4-phenanthryl)-butyric acid (II). Cyclization of this acid through its acid chloride yielded 1'-keto-1',-2',3',4'-tetrahydro-3,4-benzphenanthrene (III), which was reduced by the Clemmensen method to

(1) From the Ph.D. dissertation of R. O. Edgerton.



the corresponding tetrahydrobenzphenanthrene. The latter hydrocarbon was dehydrogenated readily to 3,4-benzphenanthrene (IV). This hydrocarbon has been synthesized previously by Cook,² by Hewett,³ and by Newman and Joshel.⁴ The cyclic ketone (III) should prove valuable for the preparation of a number of derivatives of 3,4-benzphenanthrene of interest in the field of carcinogenesis.

In the synthesis of 1-methylpyrene, 4-keto-1,2,3,4-tetrahydrophenanthrene was reduced by aluminum isopropoxide to the carbinol (V). The latter was converted to the chloride, from which



4-(1,2,3,4-tetrahydrophenanthryl)-acetic acid (VI) was prepared through the malonic ester synthesis. Cyclization of the acid through its acid chloride yielded the 1-keto-*as*-hexahydropyrene (VII). Cook⁵ cyclized the acid of I to 1-keto-

tetrahydropyrene, which he converted to pyrene. By Clemmensen reduction of VII we obtained *as*-hexahydropyrene, which was dehydrogenated to pyrene. From the reaction of VII with methylmagnesium iodide, followed by dehydration and dehydrogenation of the product, 1-methylpyrene (VIII) was obtained.

Experimental

Methyl 4-(1,2-Dihydrophenanthryl)-acetate (I).—Our procedure for carrying out the Reformatsky reaction differed somewhat from that employed by Cook.⁵ Ten grams of 4-keto-1,2,3,4-tetrahydrophenanthrene⁶ was added to a mixture of 25 g. of amalgamated zinc (20 mesh, cleansed with dilute hydrochloric acid, washed with acetone and dried), 0.2 g. of iodine and 6 cc. of methyl bromoacetate in 125 cc. of dry benzene and 125 cc. of dry ether. After the iodine color had disappeared and a yellow complex had formed, further additions of zinc and iodine were made every half-hour for two hours, and 6 cc. of methyl bromoacetate was added at the end of this time. After the reaction mixture had refluxed for two hours more, the complex was hydrolyzed with cold, dilute hydrochloric acid. The benzene-ether layer was separated and the water layer was extracted once with benzene. After the combined organic extract had been washed with dilute ammonium hydroxide several times to remove color and then with water, the solvents were removed and the crude hydroxy ester was heated with 50 cc. of anhydrous formic acid on a steam-bath for fifteen minutes. The mixture was taken up in benzene and water and the water solution extracted with benzene. After the organic layer had been washed with dilute sodium carbonate solution and with water, the solvent was removed and the residue distilled. The colorless liquid boiling at 220–225° at 1.5 mm. was collected; yield, 12.1 g. (93%).

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 81.0; H, 6.3. Found: C, 80.9; H, 6.5.

γ -(4-Phenanthryl)-butyric Acid (II).—Following the procedure of Haberland,⁷ 8.8 g. of sodium was added in portions to a boiling solution of 12 g. of the aforementioned ester in 60 cc. of absolute methanol in the course of fifteen minutes. After the vigorous reaction had subsided, 25 cc. of methanol was added and the mixture heated until all of the sodium had reacted. Then 50 cc. of water was added and the heating continued for two hours. After cooling, the mixture was acidified and extracted twice with benzene. The solution was extracted with sodium carbonate solution; acidification of this alkaline extract yielded acid which was suitable for another run. The benzene was removed and the residue distilled, the fraction boiling at 230–235° at 0.9 mm. being collected; yield, 4.32 g. The recovered acid was converted to its methyl ester by means of diazomethane and reduced in the manner described except that ethanol was substituted for methanol. In this way an additional 3.7 g. of the desired alcohol was obtained making a total yield of 75%. The compound, presumably β -[4-(1,2,3,4-tetrahydrophenanthryl)]-ethyl alcohol, was

(2) Cook, *J. Chem. Soc.*, 2524 (1931).

(3) Hewett, *ibid.*, 596 (1936).

(4) Newman and Joshel, *THIS JOURNAL*, **60**, 485 (1938).

(5) Cook, *J. Chem. Soc.*, 365 (1934).

(6) Bachmann and Edgerton, *THIS JOURNAL*, **62**, 2219 (1940).

(7) Haberland, *Ber.*, **69**, 1380 (1936).

not obtained analytically pure, but was suitable for the next step.

To a cooled solution of 4.32 g. of the aforementioned alcohol in 10 cc. of dry benzene was added 1.2 cc. of phosphorus tribromide. After standing at room temperature for two hours, the mixture was washed with water and sodium bicarbonate solution. From the latter solution phosphorous acid esters were precipitated on acidification, from which the alcohol was regenerated by alkaline hydrolysis. The benzene solution was evaporated and the residue distilled, the fraction boiling at 185–195° at 0.8 mm. being collected; yield, 3 g. (55%). The product, presumably β -[4-(1,2,3,4-tetrahydrophenanthryl)]-ethyl bromide, was not obtained quite pure.

To a solution of sodio-malonic ester prepared from 0.4 g. of sodium, 3.4 cc. of diethyl malonate and 20 cc. of absolute alcohol was added 3 g. of the aforementioned bromide. The mixture was allowed to stand at room temperature for three hours and was then refluxed for the same length of time. The solvent was removed and the residue heated with 45% potassium hydroxide solution for one hour. The crude dicarboxylic acid (2.57 g.) was heated at 160–180° for one-half hour, and the resulting acid was distilled at 1 mm. and converted to its methyl ester by means of diazomethane. The latter was heated with 0.5 g. of palladium-charcoal catalyst⁸ at 240–260° for two hours, and the product, after separation from the catalyst, was hydrolyzed by 45% potassium hydroxide solution. The γ -(4-phenanthryl)-butyric acid (0.82 g., m. p. 130–132°), after sublimation at 0.8 mm. pressure and four recrystallizations from benzene, formed colorless prisms which melted at 139.5–141°.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.0. Found: C, 82.1; H, 6.2.

1'-Keto-1',2',3',4'-tetrahydro-3,4-benzphenanthrene (III).—To a suspension of 0.6 g. of γ -(4-phenanthryl)-butyric acid in 2 cc. of ether and 1 drop of pyridine was added 0.6 cc. of thionyl chloride. After the mixture had stood at room temperature for one-half hour, the solvent and excess of reagent were removed under reduced pressure, the acid chloride was dissolved in 6 cc. of benzene and the cooled solution was treated with 0.6 cc. of anhydrous stannic chloride. After standing at room temperature for ten minutes, the mixture was hydrolyzed with ice and dilute hydrochloric acid, the benzene layer was washed twice with dilute ammonium hydroxide and then with water. After removal of the solvent, the cyclic ketone was recrystallized from alcohol, forming clusters of colorless plates (0.49 g.) which melted at 118–123°. After three recrystallizations, the ketone melted at 126.5–127.5°.

Anal. Calcd. for $C_{18}H_{14}O$: C, 87.8; H, 5.7. Found: C, 87.7; H, 5.8.

1',2',3',4'-Tetrahydro-3,4-benzphenanthrene.—A mixture of 5 g. of amalgamated zinc, 5 cc. of concentrated hydrochloric acid, 5 cc. of acetic acid, 3 cc. of toluene and 0.39 g. of the aforementioned cyclic ketone was refluxed for twenty-four hours; during this period 5 cc. each of the acids was added. The hydrocarbon obtained from the toluene layer was distilled under reduced pressure and recrystallized from alcohol, from which it was obtained in clusters of colorless needles; yield, 0.26 g. (71%); m. p. 91–93°.

(8) Zelinsky and Turowa-Pollak, *Ber.*, **58B**, 1292 (1925).

Anal. Calcd. for $C_{18}H_{16}$: C, 93.1; H, 6.9. Found: C, 93.6; H, 6.9.

The picrate crystallized from absolute alcohol in orange needles; m. p. 118–119°.

Anal. Calcd. for $C_{18}H_{16} \cdot C_6H_3N_3O_7$: N, 9.12. Found: N, 9.29.

3,4-Benzphenanthrene (IV).—A mixture of 0.15 g. of the tetrahydro derivative and 0.02 g. of palladium-charcoal catalyst was heated at 310–320° for fifteen minutes. The sides of the tube were washed down with benzene and after removal of the solvent, the dehydrogenation was continued for an additional fifteen minutes. The 3,4-benzphenanthrene crystallized from alcohol-acetone in clusters of fine, colorless needles; yield, 0.09 g. (61%); m. p. 67.5–68.3° (reported: 68°,^{2,3} 65.6–66.2° cor.⁴). The picrate melted at 128–128.5° (reported: 126–127°², 123–125°³, 122–124° cor.⁴).

4-Hydroxy-1,2,3,4-tetrahydrophenanthrene (V).—To a solution of aluminum isopropoxide, prepared by refluxing 10 g. of aluminum wire and 200 cc. of isopropyl alcohol containing 0.5 g. of mercuric chloride and 5 drops of carbon tetrachloride, was added 10 g. of 4-keto-1,2,3,4-tetrahydrophenanthrene. After the mixture had been distilled slowly until no more acetone came over, it was acidified with ice-cold 5% sulfuric acid, the carbinol was extracted with benzene, the solution washed with dilute ammonium hydroxide and evaporated. The carbinol crystallized from benzene-petroleum ether in colorless, rectangular prisms; m. p. 129–132°; yield, 8.63 g. (85%). A sample after two more recrystallizations melted at 130.5–132°. On a 2-g. run a 96% yield was obtained. Cook and Hewett⁹ reported a melting point of 140–141° for this compound, which they obtained through reduction of the cyclic ketone by Grignard reagents.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.8; H, 7.1. Found: C, 84.7; H, 7.2.

1-Keto-1,2,3,4-tetrahydrophenanthrene was reduced by aluminum isopropoxide in a similar fashion. From 2 g. of the ketone there was obtained a quantitative yield of **1-hydroxy-1,2,3,4-tetrahydrophenanthrene**. It crystallized from benzene-ligroin in clusters of colorless needles; m. p. 100–100.5°. Cook, Dodds and Lawson¹⁰ obtained this compound (m. p. 100–101°) by catalytic reduction of the ketone.

4-Chloro-1,2,3,4-tetrahydrophenanthrene.—A stream of dry hydrogen chloride was passed into a cold solution of 3 g. of the corresponding carbinol in 100 cc. of benzene containing 3 g. of anhydrous calcium chloride. After one and one-half hours, the filtered solution was evaporated and the chloride recrystallized from petroleum ether, from which it was obtained as colorless prisms; yield, 2.85 g. (86%); m. p. 75–77° with decomposition.

Anal. Calcd. for $C_{14}H_{13}Cl$: Cl, 16.4. Found: Cl, 16.3.

4-(1,2,3,4-Tetrahydrophenanthryl)-acetic Acid (VI).—A mixture of 0.6 g. of powdered sodium, 6 cc. of diethyl malonate and 50 cc. of benzene was refluxed until all of the sodium had reacted; then 2.85 g. of the aforementioned

(9) Cook and Hewett, *J. Chem. Soc.*, 398 (1933).

(10) Cook, Dodds and Lawson, *Proc. Roy. Soc. (London)*, **121B**, 133 (1936).

chloride was added. After the mixture had stood at room temperature for twelve hours, it was refluxed for two hours, the benzene was evaporated and the residue was hydrolyzed with 45% potassium hydroxide solution. The dicarboxylic acid (2.55 g.) was heated at 160–180° for one-half hour and the resulting acid (VI) was sublimed under reduced pressure (1.5 mm.) and then recrystallized from benzene-petroleum ether, from which it was obtained as colorless crystals melting at 140–141°; yield, 1.4 g. (44%, based on the chloride).

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 80.0; H, 6.6. Found: C, 80.2; H, 6.8.

1-Keto-*as*-hexahydropyrene (VII).—To a solution of 0.5 g. of the aforementioned acid, 4 cc. of ether and 1 drop of pyridine was added 0.5 cc. of thionyl chloride. After the mixture had stood at room temperature for one-half hour, the ether and excess of reagent were removed under reduced pressure, the acid chloride was dissolved in 4 cc. of benzene and the cooled solution was treated with 1 cc. of stannic chloride. After ten minutes, the mixture was hydrolyzed. The cyclic ketone crystallized from alcohol in light-yellow needles; yield, 0.42 g. (90%); m. p. 124–125.5°.

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.5; H, 6.3. Found: C, 86.4; H, 6.5.

***as*-Hexahydropyrene.**—A mixture of 5 g. of amalgamated zinc, 6 cc. of concentrated hydrochloric acid, 5 cc. of acetic acid, 4 cc. of toluene and 0.23 g. of VII was refluxed for twenty-four hours; during this time 6 cc. of hydrochloric acid and 5 cc. of acetic acid was added. The hydrocarbon obtained from the toluene layer was sublimed at 0.2 mm. and recrystallized twice from alcohol from which it was obtained as colorless leaflets; yield, 0.14 g. (65%); m. p. 104.5–106°. The picrate crystallized from alcohol in orange needles; m. p. 148.5–150°. Cook and Hewett⁹ reported a melting point of 147.5–148° for the picrate of

the hydrocarbon (m. p. 105–105.5°) which they obtained by reduction of pyrene.

A mixture of 0.1 g. of the hexahydropyrene and 0.02 g. of palladium-charcoal catalyst was heated at 300–320° for forty-five minutes. The pyrene crystallized from alcohol in colorless diamond-shaped leaflets; yield, 0.05 g. (51%); m. p. 147–148.5° alone and when mixed with authentic pyrene. The picrate of the hydrocarbon was identical with that of pyrene.

1-Methylpyrene (VIII).—To an ice-cold solution of the Grignard reagent prepared from 0.75 cc. of methyl iodide in 8 cc. of ether was added 2 cc. of benzene and 1.04 g. of the cyclic ketone. After standing overnight in the cold, the mixture was hydrolyzed. A crystalline methyl carbinol (0.98 g.) was obtained from the solution.

A mixture of 0.21 g. of the carbinol and 0.02 g. of palladium-charcoal catalyst was heated at 300–320° for one hour. The hydrocarbon after sublimation at 0.8 mm. crystallized from alcohol in colorless leaflets; yield, 0.1 g. (52%); m. p. 142–144°. After three recrystallizations, it melted at 147.5–148.5°. A mixture of the hydrocarbon and pyrene melted at 135–137° (depression).

Anal. Calcd. for $C_{17}H_{12}$: C, 94.5; H, 5.5. Found: C, 94.1; H, 5.6.

The picrate crystallized from alcohol in red needles; m. p. 226–227°. Mixed with the picrate of pyrene, the melting point was 219–222° (depression).

Anal. Calcd. for $C_{17}H_{12} \cdot C_6H_3N_3O_7$: N, 9.44. Found: N, 9.35.

Summary

The synthesis of the carcinogenic hydrocarbon 3,4-benzphenanthrene and of 1-methylpyrene from 4-keto-1,2,3,4-tetrahydrophenanthrene is described.

ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Absorption and Re-emission of Light by *cis*- and *trans*-Stilbenes and the Efficiency of their Photochemical Isomerization

BY GILBERT N. LEWIS, THEODORE T. MAGEL AND DAVID LIPKIN

For a fuller understanding of the absorption of light by complex molecules we should have more knowledge of the properties of their electronically excited states. If a substance under ordinary conditions exists in two stereoisomeric forms it is possible, when light is absorbed, that they both produce the same electronically excited molecule. In other words, in the state of electronic excitation, the two isomers may lose their individual existence and become merely phases of rotation or vibration belonging to a single state. On the other hand, it is conceivable that, even when no

isomers exist in the normal state, they may be found in a state of electronic excitation. It is, however, the first possibility with which the present paper is concerned.

Olson¹ has made a thorough theoretical study of the electronically excited states of *cis* and *trans* isomers, of the type of the substituted ethylenes; and he and his associates² have investigated experimentally several such isomeric pairs. He arrived at two main conclusions. The

(1) Olson, *Trans. Faraday Soc.*, **27**, 69 (1931).

(2) Olson and Hudson, *THIS JOURNAL*, **55**, 1410 (1933); Olson and Maroney, *ibid.*, **56**, 1820 (1934).