atomic weight analyses have contained so much colloid that the error in question is negligibly small. The only analyses about which there need be serious concern at present are two[9] which have been used to establish the ratio between silver and oxygen.

Summary

Tests of the nephelometric end-point of atomic weight titrations using saturated solutions of silver chloride have shown that the end-point of equal opalescence, although valid at room temperature, is not correct when the solutions are cooled to 0°, for at this temperature the solutions show an apparent excess of chloride over silver. Experiments made in the absence of solid silver chloride show that the apparent excess of chloride cannot be attributed to adsorption by the precipitate, but must instead be due to the fact that the opalescences of the nephelometric suspensions are not strictly proportional to the concentrations of silver and chloride in the solutions. A possible explanation for this behavior on the basis of the increased solubility of silver chloride in solutions containing excess chloride is suggested, and the effect of colloidal silver chloride on the end-point is considered briefly.

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(9) Richards and Willard, THIS JOURNAL, **32**, 48 (1910); Hönigschmid and Sachtleben, *Z. anorg. Chem.*, **178**, 1 (1929).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Studies in the Phenanthrene Series. XV. Observations on Substitution in 9,10-Dihydrophenanthrene: Tetracyclic Compounds Derived from It[1]

BY ALFRED BURGER AND ERICH MOSETTIG

The convenient method of preparation of 9,10-dihydrophenanthrene (I) recently published from this Laboratory[2] has enabled us to prepare a large number of derivatives of this hydrocarbon, which have been tested for pharmacological action.[3] In continuation of this work, the feasibility of introducing other substituents suitable for further synthetical experiments has been investigated. We have pointed out that in the Friedel–Crafts reaction on 9,10-dihydrophenanthrene the acetyl or propionyl group enters position 2 exclusively, whereas in phenanthrene itself these groups enter chiefly position 3, while position 2 is attacked only to a minor extent.[4]

2-Acetyl-9,10-dihydrophenanthrene (II), which can be prepared readily in large quantities, furnishes a convenient starting material for the preparation of the 2-amino compound by the Beckmann rearrangement of its oxime, a procedure that has been applied very recently and independently by several investigators to the preparation of phenanthryl amines.[5]

9,10-Dihydro-2-dimethylaminophenanthrene is obtained with great ease by thermal decomposition of its methiodide. 2-Hydroxy-9,10-dihydrophenanthrene may be obtained from the amino compound by means of the diazo reaction.

In the Friedel–Crafts reaction with succinic anhydride as well as in the noteworthy method of Hinkel and co-workers for introducing the aldehyde group into aromatic hydrocarbons[6] the respective substitutents enter, as was to be expected, position 2 of 9,10-dihydrophenanthrene. Whereas β-[2-(9,10-dihydrophenanthroyl)]-propionic acid (III) can be obtained in excellent yields, the yield of 9,10-dihydrophenanthrene-2-aldehyde (VI) could not be raised above 30%. In both instances no isomeric acid, or aldehyde, respectively, could be detected in the reaction mixtures. The structure of the acid (III) could be proved by synthesizing it by another route, namely, from 2-ω-bromoacetyl-9,10-dihydrophen-

(1) The work reported in this paper is part of a unification of effort by a number of agencies having responsibility for the solution of the problem of drug addiction. The organizations taking part are: The Rockefeller Foundation, the National Research Council, the U. S. Public Health Service, the U. S. Bureau of Narcotics, the University of Virginia and the University of Michigan.

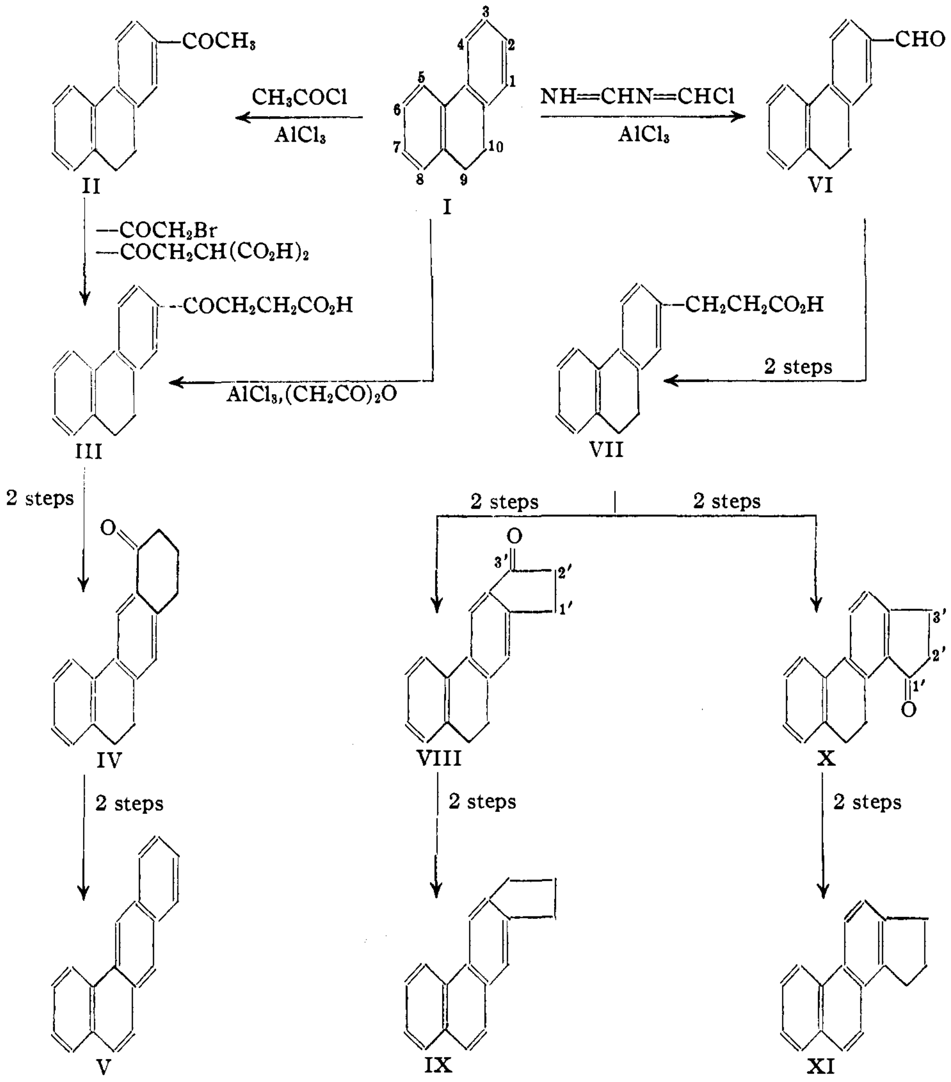
(2) (a) Burger and Mosettig, THIS JOURNAL, **57**, 2731 (1935); (b) *ibid.*, **58**, 1857 (1936). See also Durland and Adkins, *ibid.*, **59**, 135 (1937).

(3) Nathan B. Eddy, Department of Pharmacology, University of Michigan, unpublished results.

(4) Mosettig and van de Kamp, THIS JOURNAL, **52**, 3704 (1930); Bachmann and Struve, *ibid.*, **58**, 1659 (1936).

(5) Adelson and Bogert, *ibid.*, **58**, 653 (1936); Bachmann and Boatner, *ibid.*, **58**, 857, 2097 (1936); Mosettig and Krueger, *ibid.*, **58**, 1311 (1936).

(6) (a) Hinkel, Ayling and Morgan, *J. Chem. Soc.*, 2793 (1932); (b) Hinkel, Ayling and Beynon, *ibid.*, 184, 339 (1936).



anthrene and ethyl sodiomalonate. The structure of the aldehyde (VI) was ascertained by oxidation with potassium permanganate to 9,10-dihydro-2-phenanthroic acid. The keto acid III could be reduced readily with amalgamated zinc. By treating the resulting γ-[2-(9,10-dihydrophenanthryl)]-butyric acid with 85% sulfuric acid, following a method used by Haworth and co-workers in similar ring closures,[7] a cyclic ketone (IV) was obtained which, by subsequent Clemmensen reduction and selenium dehydrogenation, yielded 1,2-benzanthracene (V). This series of reactions establishes the structure of ketone IV as an 8-oxo-3,4,5,6,7,8-hexahydro-1,2-benzanthracene. No evidence of the formation of an isomeric cyclic ketone could be found. The ring closure appears to have taken place exclusively in position 3. It should be recalled that the ring closure of the analogous butyric acid derived from the unhydrogenated phenanthrene takes place in position 1, leading into the chrysene series.[7b]

9,10-Dihydrophenanthrene-2-aldehyde (VI) can be converted easily to β-[2-(9,10-dihydrophenanthryl)]-acrylic acid. The β-[2-(9,10-dihydrophenanthryl)]-propionic acid (VII) obtained by subsequent catalytic reduction yields when subjected to ring closure in the customary way[8] a mixture of the two isomeric cyclic ketones VIII and X in the approximate ratio of 5:1. They could be separated by the considerable difference in the rate of semicarbazone formation and by

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[7] (a) Haworth, *J. Chem. Soc.*, 1125 (1932); (b) Haworth and Mavin, *ibid.*, 1012 (1933).

[8] We adopted successfully the simplified technique of Adelson and Bogert, THIS JOURNAL, **59**, 399 (1937).

the different solubilities of these derivatives; the semicarbazone of 3'-oxo-9,10-dihydro-2,3-cyclopentenophenanthrene (VIII), the main product, precipitates first and is less soluble. The Clemmensen reduction of the cyclic ketone X, which appears as a by-product in the cyclization of the butyric acid derivative, and subsequent selenium dehydrogenation leads to 1,2-cyclopentenophenanthrene (XI). Hence the tetracyclic hydrocarbon obtained in the analogous way from the cyclic ketone VIII must be 2,3-cyclopentenophenanthrene (IX). Incidentally, the structures of VIII and X as 3'-oxo-9,10-dihydro-2,3-cyclopentenophenanthrene and 1'-oxo-9,10-dihydro-1,2-cyclopentenophenanthrene, respectively, appears to be established by this sequence of reactions. Here, again, it should be recalled that the analogous ring closures in the unhydrogenated phenanthrene series lead from β-(2-phenanthryl)-propionic acid[9] and from β-(2-phenanthryl)-butyric acid[10] into the 1,2-cyclopentenophenanthrene series, the ring closure apparently taking place exclusively in position 1.

Thus it may be expected in general that in the 9,10-dihydrophenanthrene series, carbon side chains attached to position 2, when forming six- and five-membered rings, will be directed entirely or chiefly to position 3, while in the phenanthrene series analogous side chains are directed from position 2 to position 1.

Experimental

2-Amino-9,10-dihydrophenanthrene.—Forty grams of the oxime of 2-acetyl-9,10-dihydrophenanthrene (m. p. 146–147.5°)[2a] was dissolved in a mixture of 80 cc. of acetic anhydride and 160 cc. of glacial acetic acid. Dry hydrogen chloride was passed into the mixture for about one hour, when a precipitate formed. The reaction mixture was allowed to stand for twenty hours. The acetylamido compound so obtained forms colorless crystals from methanol, m. p. 173–174°.

Anal. Calcd. for $C_{16}H_{15}NO$: N, 5.91. Found: N, 5.91.

For hydrolysis, the crude acetylamido compound was boiled with a mixture of 160 cc. of 6 *N* hydrochloric acid and 160 cc. of glacial acetic acid for one hour, when the amine hydrochloride crystallized out. The reaction mixture was cooled, and the precipitate was filtered and washed with a little cold water; yield, 35 g. Recrystallized from alcohol, it forms colorless leaflets, m. p. 247–257° (dec.); m. p. 323–325° (dec.) *in vacuo*.

Anal. Calcd. for $C_{14}H_{14}NCl$: C, 72.54; H, 6.10. Found: C, 72.44; H, 5.98.

The free base is oily; the picrate crystallizes from methanol in yellow needles, m. p. 203° (dec.).

Anal. Calcd. for $C_{20}H_{16}N_4O_7$: N, 13.21. Found: N, 13.14.

The amine may also be obtained by rearrangement of the oxime of 2-propionyl-9,10-dihydrophenanthrene (m. p. 129–131°)[11] in the same way. The propionylamido compound was recrystallized from alcohol, m. p. 109–110°.

Anal. Calcd. for $C_{17}H_{17}NO$: N, 5.58. Found: N, 5.39.

2-Dimethylamino-9,10-dihydrophenanthrene.—Eight and three-tenths grams of 2-amino-9,10-dihydrophenanthrene was shaken with an excess of dimethyl sulfate and a 10% aqueous solution of potassium hydroxide for two to three hours, the reaction mixture being kept alkaline. A small amount of crystalline tertiary amine was filtered out and an excess of potassium iodide was added to the filtrate. The white crystalline methiodide was collected, dried and, without further purification, subjected to heat decomposition in a vacuum. The distillate was dissolved in ether, the ether solution was extracted with aqueous dilute hydrochloric acid, and the amine was precipitated from the acid solution with dilute alkali. It was recrystallized from dilute alcohol, colorless leaflets, m. p. 65–66°; yield 80%.

Anal. Calcd. for $C_{16}H_{17}N$: N, 6.28. Found: N, 6.19.

The hydrochloride crystallized from alcohol–ether as felted needles, m. p. 186–188°. It may be sublimed in a high vacuum at 80–120° without any appreciable dissociation. Traces of free base were removed by washing the sublimate with dry ether.

Anal. Calcd. for $C_{16}H_{18}NCl$: C, 73.96; H, 6.99. Found: C, 74.03; H, 6.75.

2-Hydroxy-9,10-dihydrophenanthrene.—Three grams of 2-amino-9,10-dihydrophenanthrene hydrochloride was suspended in 50 cc. of 1 *N* sulfuric acid and diazotized at 2° with a solution of 0.9 g. of sodium nitrite in 50 cc. of water. The solution was stirred at 10° for forty minutes, filtered, diluted with 100 cc. of water, and heated to boiling. The phenol was purified by distillation in a high vacuum and recrystallization from benzene–petroleum ether; yield 1 g., m. p. 111.5–113°.

Anal. Calcd. for $C_{14}H_{12}O$: C, 85.67; H, 6.17. Found: C, 85.59; H, 6.59.

The methoxy and acetoxy derivatives were oily.

9,10-Dihydrophenanthrene-2-aldehyde (VI).—The reaction was carried out following closely the experimental directions of Hinkel, Ayling and Beynon.[6b] In a three-necked flask equipped with a reflux condenser, a dropping funnel and a delivery tube, 81 g. of aluminum chloride was suspended in 300 cc. of dry chlorobenzene. The mixture was cooled in ice water, and 36 cc. of anhydrous hydrogen cyanide was added with frequent shaking in the course of twenty minutes. The mixture was kept at room temperature for fifteen minutes with frequent shaking, 54 g. of 9,10-dihydrophenanthrene was added, and hydrogen chloride was passed in slowly for fifteen minutes. The mixture was then heated in a water-bath at 55° for three hours and at 60° for another three hours while hydrogen chloride was

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[9] Bachmann, This Journal, **57**, 1381 (1935).

[10] Hillemann, *Ber.*, **69**, 2610 (1936).

[11] Burger and Mosettig, This Journal, **58**, 1857 (1936).

passed through continually. The pasty mass was decomposed with ice and concentrated hydrochloric acid, the ice was allowed to melt, and the chlorobenzene was removed with steam. The resulting light brown oil was extracted into ether and the aldehyde was isolated through the bisulfite compound. It formed a light yellow oil which was purified by distillation in a vacuum, b. p. 185° (2 mm.); yield 18 g.

Anal. Calcd. for $C_{15}H_{12}O$: C, 86.50; H, 5.82. Found: C, 86.44; H, 5.95.

The non-aldehydic reaction products formed a red oil which was distilled in a vacuum. Chromic acid oxidation of the light yellow distillate and selenium dehydrogenation indicated that it consisted largely of unchanged 9,10-dihydrophenanthrene.

The semicarbazone is sparingly soluble in alcohol; colorless, m. p. 235–236° (dec.).

Anal. Calcd. for $C_{16}H_{15}N_3O$: N, 15.85. Found: N, 16.04.

The *p*-nitrophenylhydrazone is formed by mixing the components in cold glacial acetic acid. It crystallized from hot *n*-butyl alcohol as red needles, m. p. 242–244° (dec.).

Anal. Calcd. for $C_{21}H_{17}N_3O_2$: N, 12.25. Found: N, 12.57.

Structural Proof of Aldehyde.—The aldehyde was oxidized with potassium permanganate in acetone solution according to Head and Robertson.[12] The resulting acid melted at 211–213° and was identical with 9,10-dihydro-2-phenanthroic acid (mixed melting point). Moreover the melting points of the amides of the two acids showed no depression.

The amide was prepared from the acid chloride with ammonia in benzene solution. It was recrystallized from dilute alcohol; colorless needles, m. p. 180–181°.

Anal. Calcd. for $C_{15}H_{13}NO$: N, 6.28. Found: N, 5.97.

9,10-Dihydrophenanthryl-2-carbinol.—The aldehyde was hydrogenated smoothly in alcoholic solution in the presence of a platinum oxide catalyst. The carbinol is very soluble in the usual organic solvents and crystallized in long needles from ether–petroleum ether; m. p. 77–78°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.67; H, 6.71. Found: C, 85.44; H, 6.66.

The α-naphthylurethan forms small colorless needles from alcohol, m. p. 145–146°.

Anal. Calcd. for $C_{26}H_{21}NO_2$: N, 3.70. Found: N, 3.78.

β-[2-(**9,10-Dihydrophenanthroyl**)]-**propionic Acid** (III).—(A) A solution of 50 g. of aluminum chloride in 80 cc. of dry nitrobenzene was added to a mixture of 34 g. of 9,10-dihydrophenanthrene, 20 g. of succinic anhydride and 70 cc. of nitrobenzene at 0°. The mixture was allowed to stand at 0° for three hours, then at room temperature for eighteen hours, and was worked up in the customary way. The crude reaction product weighed 52 g. and was used in the Clemmensen reduction. It was recrystallized from dilute alcohol and formed colorless needles, m. p. 157.5–158.5°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.11; H, 5.76. Found: C, 76.92; H, 5.54.

(B) Powdered sodium (0.4 g.) was covered with a solution of 2.7 g. of diethylmalonate and 5 g. of 2-bromoacetyl-9,10-dihydrophenanthrene in 50 cc. of dry benzene. The solution became hot and was boiled under reflux for seven hours. A small amount of unreacted sodium was destroyed by addition of a few drops of alcohol, dilute hydrochloric acid was added and the benzene layer was separated, washed and evaporated. The ester was saponified with a 5% solution of alcoholic potassium hydroxide, and the free dicarboxylic acid was decarboxylated at 155–160°. The acid was purified by reprecipitation and recrystallization from dilute alcohol; yield 60%, m. p. 155–156°. A mixed melting point with the acid prepared by method (A) showed no depression.

γ-[2-(**9,10-Dihydrophenanthryl**)]-**butyric Acid.**—Fifty-two grams of the keto acid was boiled with 104 g. of amalgamated zinc, 208 cc. of concentrated hydrochloric acid, 78 cc. of water, 5 cc. of glacial acetic acid and 2.5 cc. of toluene for forty-five hours, 100 cc. of hydrochloric acid being added after ten hours and then again after thirty hours.[13] The acid was worked up in the usual way and purified by distillation in a high vacuum; yield 85%. It was obtained from a mixture of benzene and petroleum ether as colorless, silky needles, m. p. 92°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.16; H, 6.82. Found: C, 81.32; H, 7.23.

8-Oxo-3,4,5,6,7,8-hexahydro-1,2-benzanthracene (IV).—Twenty grams of the above butyric acid derivative was added to 160 cc. of hot 85% sulfuric acid and stirred on a steam-bath for forty-five minutes. The reaction mixture was worked up in the customary way.[7] The ketone was purified through the semicarbazone, from which it can be recovered easily by boiling with 6 *N* hydrochloric acid for twenty minutes. Distillation in a high vacuum and recrystallization from methanol yielded needles, m. p. 97–98° (30% yield).

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.05; H, 6.50. Found: C, 86.68; H, 6.68.

The semicarbazone crystallized in colorless felted needles from alcohol, m. p. 277–279° (dec., *in vacuo*).

Anal. Calcd. for $C_{19}H_{19}N_3O$: N, 13.77. Found: N, 13.75.

The oxime crystallizes in colorless prisms from alcohol, m. p. 197–198°.

Anal. Calcd. for $C_{18}H_{17}NO$: N, 5.32. Found: N. 5.39.

1,2-Benzanthracene (V).—One gram of the semicarbazone was heated in a sealed tube with a solution of 0.2 g. of sodium in 5 cc. of absolute alcohol to 170–180° for eight hours. After removal of the alcohol the hydrocarbon was extracted into ether. It was purified by distillation in a high vacuum; light yellow oil, forms no picrate.

One gram of the hexahydrobenzanthracene was heated with 2 g. of selenium at 290–315° for sixty hours in a sealed tube. The ether extract of the reaction mixture was washed with dilute alkali and the crystalline residue from the ether solution was distilled in a high vacuum and

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[12] Head and Robertson, *J. Chem. Soc.*, 2432 (1931).

[13] See Martin, THIS JOURNAL, 58, 1438 (1936).

recrystallized from alcohol; glittering leaflets, m. p. 156–157°, yield nearly quantitative.

Anal. Calcd. for $C_{18}H_{12}$: C, 94.69; H, 5.31. Found: C, 94.61; H, 5.50.

The 1,2-benzanthracenequinone, obtained by oxidation with chromic acid in glacial acetic acid, melts at 164–165°. The picrate melts at 138–140°.

Previous investigators[7b,14] described 1,2-benzanthracene as colorless plates, m. p. 155–157°; the picrate, m. p. 142–143°, and the quinone, m. p. 165–167°, while chrysene melts at 251–252° and chrysenequinone at 239°.

β-[2-(9,10-Dihydrophenanthryl)]-acrylic Acid.—A solution of 4 g. of 9,10-dihydrophenanthrene-2-aldehyde and 5 g. of malonic acid in 12 cc. of dry pyridine and 0.4 cc. of piperidine was heated on a steam-bath for one hour.[15] The reaction was completed by heating the mixture to boiling for five minutes. The acrylic acid derivative was purified by recrystallization from methyl ethyl ketone. For analysis, it was purified by sublimation in a high vacuum and crystallization from alcohol (sparingly soluble); fine, colorless needles, m. p. 221–223°, yield, 80%.

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.59; H, 5.89.

β-[2-(9,10-Dihydrophenanthryl)]-propionic Acid (VII).—The acrylic acid derivative, suspended in 25 parts of alcohol, could be hydrogenated quantitatively in the presence of platinum oxide. The propionic acid derivative was recrystallized from dilute alcohol; glittering leaflets, m. p. 153–154°.

Anal. Calcd. for $C_{17}H_{16}O_2$: C, 80.91; H, 6.40. Found: C, 81.04; H, 6.54.

3′-Oxo-9,10-dihydro-2,3-cyclopentenophenanthrene (VIII), and 1′-Oxo-9,10-dihydro-1,2-cyclopentenophenanthrene (X).—The ring closure of β-[2-(9.10-dihydrophenanthryl)]-propionic acid was carried out in the simplified manner used recently by Adelson and Bogert in a similar case.[8] A solution of 10 g. of the propionic acid and 9 g. of phosphorus pentachloride in 100 cc. of dry benzene was heated for one hour. Nine grams of aluminum chloride was added gradually to the cooled solution with stirring, and a green precipitate was formed with evolution of gas. The mixture was stirred for thirty minutes at room temperature, then heated to boiling for one and one-half hours, and worked up in the usual manner; yield of crude ketones, 97%. The mixture was distilled in a high vacuum, dissolved in 300 cc. of alcohol and boiled with a solution of 5 g. of semicarbazide hydrochloride and 5.5 g. of sodium acetate in 5 cc. of water for ten minutes. At this point, the main part of the semicarbazone of VIII had precipitated in a pure state and was filtered from the hot solution. A second crop of semicarbazone was collected when the solution had cooled to 30°. It consisted mainly of the semicarbazone of VIII. The mother liquor was allowed to stand overnight and deposited the semicarbazone of X in the form of long fine needles. The semicarbazones could be hydrolyzed easily by boiling with 6 *N* hydrochloric acid.

The ketone VIII (yield, 5.6 g.), after distillation in a high vacuum and crystallization from alcohol, forms long colorless needles, m. p. 131–132°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.14; H, 6.03. Found: C, 87.11; H, 6.03.

The semicarbazone is sparingly soluble in alcohol and forms small, whetstone-shaped colorless crystals, m. p. 261–263° (dec., *in vacuo*).

Anal. Calcd. for $C_{18}H_{17}N_3O$: N, 14.43. Found: N, 14.71.

The oxime is very sparingly soluble in alcohol; colorless, whetstone-shaped prisms, m. p. 243–245° (dec.).

Anal. Calcd. for $C_{17}H_{15}NO$: N, 5.62. Found: N, 5.91.

Ketone X (yield 1.2 g.) was purified by distillation in a high vacuum and crystallization from alcohol; colorless, large transparent plates, m. p. 143–144°.

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.14; H, 6.03. Found: C, 87.51; H, 6.39.

The semicarbazone forms very slowly. Recrystallized from boiling alcohol, it forms fine colorless needles, m. p. 263–268° (dec., *in vacuo*).

Anal. Calcd. for $C_{18}H_{17}N_3O$: N, 14.43. Found: N, 14.69.

The mixed melting point of the semicarbazones of VIII and X showed a depression of 20–30°. The mixed melting point of the ketones was at 105–110°.

2,3-Cyclopentenophenanthrene (IX).—One gram of 3′-oxo-9,10-dihydro-2,3-cyclopentenophenanthrene was boiled with 10 g. of amalgamated zinc, 40 cc. of concentrated hydrochloric acid, 6 cc. of water, 2 cc. of toluene and a drop of glacial acetic acid for twenty-four hours. The reaction mixture was extracted with ether, and the crude hydrocarbon was obtained by distillation in a high vacuum as a colorless oil which gave no picrate.

For dehydrogenation, the crude 9,10-dihydro-2,3-cyclopentenophenanthrene was heated with 2 g. of selenium in a sealed tube at 300–310° for eighteen hours. The reaction mixture was worked up as in the case of 1,2-benzanthracene. The 2,3-cyclopentenophenanthrene was recrystallized from methanol and formed needle-like prisms of m. p. 84–84.5°. It shows no fluorescence in alcoholic solution.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 93.41; H, 6.60.

The picrate forms orange needles from methanol, m. p. 156–157° (dec.).

Anal. Calcd. for $C_{23}H_{17}N_3O_7$: N, 9.40. Found: N, 9.30.

The styphnate crystallizes from alcohol in yellow needles, m. p. 158–159°.

Anal. Calcd. for $C_{23}H_{17}N_3O_8$: N, 9.07. Found: N, 8.93.

1,2-Cyclopentenophenanthrene (XI).—Three-tenths of a gram of 1′-oxo-9,10-dihydro-1,2-cyclopentenophenanthrene (X) was reduced by the Clemmensen method as described in the case of the isomer. The resulting 9,10-dihydro-1,2-cyclopentenophenanthrene was purified by distillation in a high vacuum and crystallization from

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[14] Cook, *J. Chem. Soc.*, 2524 (1931).

[15] This reaction was carried out by the modified Knoevenagel reaction. See Haworth, Perkin and Rankin, *J. Chem. Soc.*, **125**, 1693 (1924); Robinson and Shinoda, *ibid.*, **127**, 1979 (1925).

methanol; colorless leaflets, m. p. 65–69°. This hydrocarbon was dehydrogenated with selenium at 300° for sixteen hours without any further purification. 1,2-Cyclopentenophenanthrene crystallized from methanol in colorless prisms, m. p. 133–134°. It showed no fluorescence in alcoholic solution.

Anal. Calcd. for $C_{17}H_{14}$: C, 93.53; H, 6.47. Found: C, 92.98, 93.00; H, 6.38, 6.53.

The picrate crystallized from methanol; orange needles, m. p. 131–132°.

Previous investigators[16] found physical properties as follows:

Reference	1,2-Cyclopentenophenanthrene, m. p., °C.	Picrate, m. p., °C.
a	135–136	133–134
b	134.5–135	134.5–135
c	134–135	133–134

Summary

The preparation of 2-amino- and 2-hydroxy-9,10-dihydrophenanthrene from 2-acetyl-9,10-dihydrophenanthrene is described.

β-[2-(9,10-Dihydrophenanthryl)]-butyric acid and β-[2-(9,10-dihydrophenanthryl)]-propionic acid have been subjected to ring closure. In the first case the ring closure takes place, as far as can be determined, in position 3 only; in the second case the ring closure in position 3 is the main reaction, and ring closure in position 1 occurs to a minor extent only. The course of the reactions has been confirmed through characterization of the tetracyclic hydrocarbons, benzanthracene and the cyclopentenophenanthrenes, respectively, obtained from the primarily-formed cyclic ketones.

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[16] (a) Kon, *J. Chem. Soc.*, 1087 (1933); (b) Cook and Hewett, *ibid.*, 1109 (1933); (c) Ruzicka, Ehmann, Goldberg and Hösli, *Helv. Chim. Acta*, **16**, 835 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Preparation and Some Reactions of 1-Halogenoalkynes[1]

BY P. A. MCCUSKER AND R. R. VOGT

As a preliminary to a study of the reactions of the 1-halogenoalkynes, various methods for the preparation of these compounds were investigated. Satisfactory methods are available for the preparation of the iodo compounds, by the iodination of the sodium alkyl acetylides, as reported by Vaughn and Nieuwland,[2] and by the iodination of the alkynylmagnesium halides, as reported by Grignard and Perrichon.[3]

For the preparation of the 1-bromoalkynes the reaction of cyanogen bromide with the acetylenic Grignard reagent has been used by Grignard, Bellet and Courtot.[4] The method of Strauss[5] gives high yields of phenylbromoacetylene but the reaction is slow in the alkyl series. For the preparation of the 1-chloroalkynes this method has not been satisfactory. The only method available for the systematic preparation of the 1-chloroalkynes has been that of Truchet.[6]

Jositsch[7] has prepared phenylbromoacetylene by bromination of the Grignard derivative at low temperatures but did not state his yields nor extend the method to the alkyl series. Modifications of this method of low temperature halogenation of metal alkyl acetylides have been studied and found to be suitable for the preparation of 1-chloro- and 1-bromoalkynes.[8] When the temperature of the reaction mixture is kept low enough, the free halogen can, in certain instances, be made to replace the metal of the metal alkyl acetylide without appreciable polymerization or addition taking place. The preparation of 1-bromo- and 1-chloroheptyne by such a procedure is described in the experimental part.

A number of other chlorinating agents were tried for the preparation of the 1-chloroalkynes. Tertiary butyl hypochlorite, thionyl chloride, calcium hypochlorite and dichloramine T gave little or no chloroalkyne on reaction with the alkali metal or magnesium derivatives of the alkyl acetylenes.

A study of the reactions of the 1-bromoalkynes has been made by Grignard and Perrichon[3] and Truchet[6] has investigated the 1-chloroalkynes. The strength of the carbon–halogen bond in all these compounds is noteworthy. No reactions of

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[1] Paper No. XXI on the chemistry of the alkyl acetylenes and their addition products; previous paper, THIS JOURNAL, **59**, 855 (1937).

[2] Vaughn and Nieuwland, *ibid.*, **55**, 2150 (1933).

[3] Grignard and Perrichon, *Ann. chim.*, **5**, 5–36 (1926).

[4] Grignard, Bellet and Courtot, *ibid.*, **4**, 30 (1915).

[5] Strauss, Kolleck and Heyn, *Ber.*, **63B**, 1868 (1930).

[6] Truchet, *Ann. Chim.*, **16**, 309 (1931).

[7] Jositsch, *Bull. soc. chim.*, [3] **34**, 184 (1905).

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