separated as orange needles, m.p. 112–118°, yield 0.36 g. (60% based on the original oxide employed). Recrystallization from ethanol raised the melting point of the derivative to 120–121°. The product was shown to be identical with an authentic sample of methyl isopropyl ketone 2,4-

dinitrophenylhydrazone and to differ from the corresponding derivative of acetone by the criteria previously described. We were unable to isolate any other product from the crude pyrolysis product.

CAMBRIDGE 39, MASSACHUSETTS

The Chlorination of 3-Phenanthrol

BY CHARLES K. BRADSHER, FRANCES C. BROWN AND PRESTON H. LEAKE[1]

The chlorination of 3-phenanthrol with one equivalent of sulfuryl chloride yielded 4-chloro-3-phenanthrol, while with two equivalents, 4,9-dichloro-3-phenanthrol was produced. Four equivalents afforded a neutral compound believed to be 1,2,4,4,9-pentachloro-3-keto-1,2,3,4-tetrahydrophenanthrene (XIII). Reductive dehydrohalogenation of XIII yielded 2,4,9-trichlorophenanthrol. None of the chlorinated 3-phenanthrols proved superior to the parent substance in activity toward A. niger or E. coli.

Of more than eighty phenanthrene derivatives tested for fungistatic activity against *Aspergillus niger*, Steinberg[2] found 3-phenanthrol to be most effective. Subsequently[3] it was demonstrated that comparable fungitoxicity was shown by several congeners including related fluorenols and hydroxybiphenyls. The observation that the fungitoxicity of phenol[4] and of 2-naphthol[5] was increased by the introduction of one or more chlorine atoms suggested that it might be of interest to prepare and test some chlorinated 3-phenanthrols.

The chlorination of 3-phenanthrol (I) has been investigated in a preliminary way by Fieser and Dunn[6] using an excess of elementary chlorine. The product was described as probably 1,4,4-trichloro-3-keto-3,4-dihydrophenanthrene-9,10-dichloride (II) since on reductive dehydrohalogena-

I   II   III

tion with stannous chloride it yielded an acidic compound which on the basis of its reactions was described as "1(?),4,9(or 10)-trichloro-3-phenanthrol"(III).

For greater convenience, sulfuryl chloride was used in our studies. When one equivalent was allowed to react with I, a monochlorination product was obtained. By analogy with the chlorination of 2-naphthol[7] it would be anticipated that the chlorine was at position 4. Strong support for this

formulation was afforded by the failure of the chlorophenanthrol to undergo diazonium coupling when treated with diazotized sulfanilic acid. The characteristic ease with which 1-halo-2-naphthols undergo reductive dehalogenation when treated with tin and hydrochloric acid,[8] was likewise shown by our new chlorophenanthrol which under the same conditions, afforded 3-phenanthrol in 91% yield. It was shown that 3-methoxyphenanthrene gave similar orientation in the chlorination reaction with sulfuryl chloride. The new ether, when subjected to the conditions of the Rosenmund–von Braun reaction, yielded a nitrile IV. Refluxing the nitrile with 35% potassium hydroxide solution

$$3\text{-}CH_3O\text{-}4Cl\text{-}C_{14}H_8 \xrightarrow{\text{CuCN}}$$

$$3\text{-}CH_3O\text{-}4CN\text{-}C_{14}H_8 \xrightarrow{\text{KOH}} 3\text{-}OH\text{-}4\text{-}CN\text{-}C_{14}H_8$$

$$\text{IV} \qquad\qquad\qquad \text{V}$$

gave the hydroxy nitrile V[9] rather than the amide or acid. The unreactivity of the nitrile group can be explained in terms of the steric hindrance expected at the 4-position of a 3-substituted phenanthrene.

Chlorination of 3-phenanthrol with two equivalents of sulfuryl chloride or of 4-chloro-3-phenanthrol with one equivalent yielded a dichloro-3-phenanthrol. In this instance analogy with 2-naphthol is not particularly helpful. In the latter case the consensus is that the dichlorination product is 1,1-dichloro-2(1H)-naphthalenone (VI).[10]

VI   VII

(1) Allied Chemical and Dye Corporation Fellow 1953–1954. This work was supported in part by the Chemical Corps, Fort Detrick, Maryland, under contract with Duke University.

(2) R. A. Steinberg, *J. Agr. Research*, **60**, 765 (1940).

(3) C. K. Bradsher, F. C. Brown and H. K. Porter, THIS JOURNAL, **76**, 2357 (1954).

(4) I. Hatfield, *Proc. Am. Wood-Preservers' Assoc.*, **31**, 57 (1935).

(5) H. B. S. Montgomery and M. H. Moore, *J. Pomol. Hort. Sci.*, **15**, 253 (1938). Also unpublished results from this Laboratory.

(6) L. F. Fieser and J. T. Dunn, THIS JOURNAL, **59**, 1024 (1937).

(7) Position 4 of 3-phenanthrol is structurally related to position 1 of 2-naphthol. It was demonstrated by T. Zincke that 2-naphthol chlorinates in the 1-position; *Ber.*, **21**, 1027 (1888).

(8) *E.g.*, H. Franzen and G. Stauble, *J. prakt. Chem.*, [2] **103**, 352 (1921–22); K. Fries and K. Schimmelschmidt, *Ber.*, **58**, 2835 (1925).

(9) Other instances of ether cleavage by alkali are known, *e.g.*, E. C. Dodds, *Proc. Roy. Soc. (London)*, **B132**, 88 (1944), although the present case might be considered a nucleophilic displacement by hydroxide ion, to be compared with the displacement of *ortho* methoxyl groups from sterically hindered ketones by the Grignard reagent; R. C. Fuson and S. B. Speck, THIS JOURNAL, **64**, 2446 (1942).

(10) (a) T. Zincke, *Ber.*, **21**, 3378, 3540 (1888); (b) K. Fries and K. Schimmelschmidt, *Ann.*, **484**, 245 (1930); (c) P. M. James and D. Woodcock, *J. Chem. Soc.*, 1931 (1951).
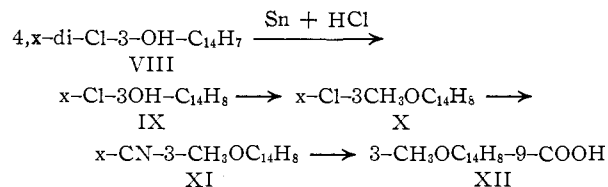
The claim[11] that chlorination of 1-chloro-2-naphthol yields 1,6-dichloro-2-naphthol has not been confirmed by subsequent investgators.[10c] The issue is further confused by the observation that chlorination with *sulfuryl chloride* instead of chlorine afforded 1,4-dichloro-2-naphthol (VII).[12]

Our 4,x-dichloro-3-phenanthrol VIII was easily reduced to a new x-chloro-3-phenanthrol IX, which

$$4,x\text{-di-Cl-3-OH-C}_{14}H_7 \xrightarrow{\text{Sn + HCl}}$$
$$\text{VIII}$$

$$x\text{-Cl-3OH-C}_{14}H_8 \longrightarrow x\text{-Cl-3CH}_3OC_{14}H_8 \longrightarrow$$
$$\text{IX} \qquad\qquad \text{X}$$

$$x\text{-CN-3-CH}_3OC_{14}H_8 \longrightarrow 3\text{-CH}_3OC_{14}H_8\text{-9-COOH}$$
$$\text{XI} \qquad\qquad\qquad \text{XII}$$

was etherified (X) and converted to the nitrile XI by heating with cuprous cyanide. Hydrolysis of the nitrile afforded the known 3-methoxyphenanthrene-9-carboxylic acid XII[13] demonstrating that VIII was actually 4,9-dichloro-3-phenanthrol. It was shown that the orientation of 3-methoxyphenanthrene was similar, affording 3-methoxy-4,9-dichlorophenanthrene.

When 3-phenanthrol was treated with four equivalents of sulfuryl chloride it afforded a neutral, yellow compound melting at 199–200° with decomposition. Since this substance could be obtained also by the action of two equivalents of sulfuryl chloride on 4,9-dichloro-3-phenanthrol it seemed most likely that it had the formula XIII, analogous (as regards the terminal ring) to the chlorination

XIII   XIV   XV
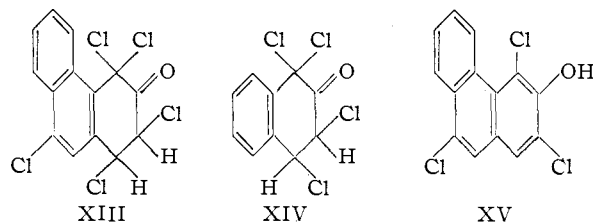
product XIV from 2-naphthol.[10a] It appears probable that XIII is also the pentachloro derivative of Fieser and Dunn[6] since we found that direct chlorination of 3-phenanthrol with chlorine yielded the same product as that obtained with sulfuryl chloride.

Reductive dehydrohalogenation of the pentachloro compound XIII using stannous chloride afforded a trichlorophenanthrol which differed significantly in its properties and reactions from that obtained by Fieser and Dunn.[6] Since it has been shown that, depending upon the conditions, the action of stannous chloride on 1,1,3,4-tetrachloro-2-tetralone (XIV) will yield 1,4-dichloro-2-naphthol and/or 1,3-dichloro-2-naphthol[7] it appears plausible that XIII might give rise to two trichlorophenanthrols. Since Fieser and Dunn[6] have presented good evidence that their product has a chlorine atom at position 1, by analogy their compound should be 1,4,9-trichloro-3-phenanthrol, and ours 2,4,9-trichloro-3-phenanthrol (XV).

(11) P. Ruggli, K. Knapp, E. Merz and A. Zimmermann, *Helv. Chim. Acta*, **12**, 1034 (1929).

(12) H. E. Armstrong and E. C. Rossiter, *Proc. Chem. Soc.*, **7**, 32 (1889); *Chem. News*, **63**, 136 (1889); H. Burton. *J. Chem. Soc.*, 280 (1945).

(13) E. Mosettig and A. Burger, THIS JOURNAL, **55**, 2981 (1953).

Reduction of XV yielded the new 2,9-dichloro-3-phenanthrol (XVI). When either XV or XVI was

XVI   XVII   XVIII
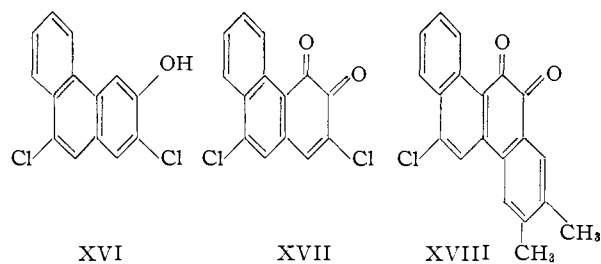
oxidized with nitric acid a dichloroquinone XVII was obtained. It might be anticipated by analogy to the behavior of 2-bromo-3,4-phenanthrenequinone that XVII would undergo the Diels–Alder reaction with 2,3-dimethylbutadiene.[6] As judged from the change in color of the chloroform solution of the quinone, reaction was rapid at 100°. The adduct was not isolated as such, but treated with sodium acetate in acetic acid solution to yield an orange-red quinone XVIII having an ultraviolet absorption spectrum similar to that of chrysenequinone.

More direct evidence concerning the location of the chlorine atom in the quinone ring was afforded by the Thiele reaction. It has been shown[14] that 3-chloro-1,2-naphthoquinone enters into the Thiele reaction normally, affording 3-chloro-1,2,4-triacetoxynaphthalene, while 4-chloro-1,2-naphthoquinone is recovered unchanged under the same conditions.[15] Our dichloro - 3,4 - phenanthrenequinone when treated with acetic anhydride and sulfuric acid reacted *without loss of chlorine to yield a triacetate*.[16] While it was logical to suppose that the new triacetate had the structure XIX, it seemed wise to demonstrate the position of the acetoxyl

XIX   XX   XXI
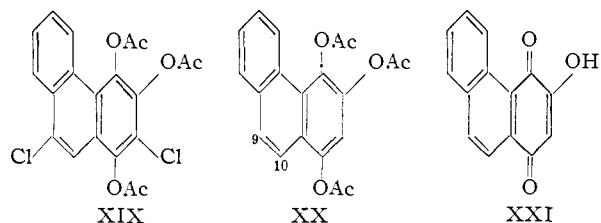
groups. Hydrogenation of XIX, using a palladium catalyst in the presence of sodium acetate, afforded a chlorine-free product melting within one degree of the reported melting point of 1,3,4-triacetoxyphenanthrene (XX). A mixed melting point determination with an authentic sample[17] showed a large melting point depression. From the carbon and hydrogen analysis and the ultraviolet absorption spectrum it appeared most probable that our reduction product was a 9,10-dihydro derivative. Attempted dehydrogenation using nitrobenzene, chloranil and palladium-on-charcoal afforded resinous or impure products. It was found

(14) L. F. Fieser and C. K. Bradsher. *ibid.*, **61**, 417 (1939).

(15) Fieser and Dunn (ref. 6) have shown that 2-bromo-3,4-phenanthrenequinone undergoes the Thiele reaction.

(16) Fieser and Dunn found that their trichlorophenanthrol III gave a quinone (isomeric with XVII) which underwent the Thiele reaction with *elimination* of chlorine.

(17) We are indebted to Prof. Louis F. Fieser for this sample.

that dehydrogenation could be effected by hydrolysis of the 1,3,4-triacetoxy-9,10-dihydrophenanthrene followed by air oxidation to yield the quinone XXI.[18] Reductive acetylation of the hydroxyketone XXI afforded the 1,3,4-triacetoxyphenanthrene of Fieser.[19]

Another observation worthy of mention is that o-phenylenediamine reacts with the dichlorophenanthrenequinone XVII in an anomalous fashion, yielding a compound having the composition expected for $C_{26}H_{13}N_4Cl$. Since one chlorine has been lost in this condensation, and reaction of an aromatic amine with the quinoid system would be expected to occur at position-1[20] the structure XXII is proposed for this product.
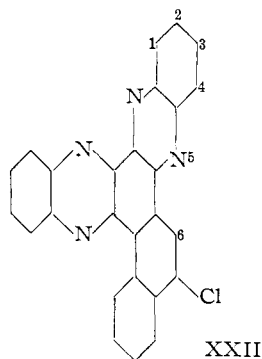
XXII

The chlorinated 3-phenanthrols were tested for activity against the saprophytic fungus *Aspergillus niger* and the gram-positive and gram-negative bacteria *B. subtilis* and *E. coli*.[21] The results of these tests are recorded in Table I. It is clear

TABLE I

ANTIMICROBIAL TESTING RESULTS

Name	Inhibition, % at 250 p.p.m. A. niger	Lowest lethal concn., p.p.m. E. coli	B. subtilis
3-Phenanthrol	100[a]	100	50
4-Chloro-3-phenanthrol	43	>250	25
9-Chloro-3-phenanthrol	100[b]	>250	10
2,9-Dichloro-3-phenanthrol	12	>250	>250
4,9-Dichloro-3-phenanthrol	6	>250	200
2,4,9-Trichloro-3-phenanthrol	15	>250	>250

[a] This compound was also effective at higher dilution: 200, 100; 100, 100; 50, 100; 25, 50; 10, 40. [b] This compound was also effective at higher dilution: 200, 91; 100, 84; 50, 73; 25, 61; 10, 51.

that against *A. niger* the introduction of chlorine into the 9-position is without benefit and in the 2- and 4-positions actually results in a decrease in activity. Monochlorination improved slightly the bacteriostatic activity toward *B. subtilis* but decreased markedly the activity toward *E. coli*. The decrease in activity uniformly observed when

two or more chlorine atoms are present may be caused by decreased water solubility.[22]

Experimental[23]

Absorption Spectra.—The ultraviolet absorption spectra were determined in 95% ethyl alcohol solution, using a Beckman model DU quartz spectrophotometer with one-centimeter silica cells.

3-Phenanthrol.—This material was prepared from the corresponding sulfonic acid salt by potassium hydroxide fusion. Phenanthrene-3-sulfonic acid was prepared in the manner described by Fieser,[24] and the subsequent fusion was carried out essentially as described by Werner.[25]

4-Chloro-3-phenanthrol.—Three and nine-tenths grams (0.02 mole) of 3-phenanthrol was dissolved in 15 ml. of glacial acetic acid with warming. To this solution at room temperature was added 2.7 g. (0.02 mole) of sulfuryl chloride. After two hours, the crystalline product was collected; weight 3.5 g. (77%), m.p. 108–111°. An additional small amount of less pure material was obtained from the filtrate. The analytical sample crystallized from dilute ethanol as white needles, m.p. 113–113.5°.

Anal. Calcd. for $C_{14}H_9ClO$: C, 73.53; H, 3.97; Cl, 15.51. Found: C, 73.33; H, 4.04; Cl, 16.06.

4-Chloro-3-phenanthrol is soluble in dilute sodium hydroxide. The basic solution becomes only slightly pink when treated with diazotized sulfanilic acid.

3-Methoxy-4-chlorophenanthrene. (a) By the Methylation of 4-Chloro-3-phenanthrol.—The methyl ether of 7.3 g. of 4-chloro-3-phenanthrol was prepared according to the general methylation procedure of Buck.[26] After recrystallizing the product once from methanol, there was obtained 6.4 g. of white needles, m.p. 91–93°. The analytical sample melted at 92.5–93°.

Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57. Found: C, 73.90; H, 4.65.

(b) By the Chlorination of 3-Methoxyphenanthrene.—Two hundred and fifty milligrams (1.2 mmoles) of 3-methoxyphenanthrene in 1 ml. of glacial acetic acid was treated with 0.163 g. (1.2 mmoles) of sulfuryl chloride at room temperature during one hour. The solvent was evaporated under a stream of air and the residue was crystallized from methyl alcohol, m.p. 89–91°; weight 230 mg. This material gave no melting point depression when it was mixed with that from (a) above.

3-Methoxy-4-cyanophenanthrene (IV).—One and one-tenth grams of 3-methoxy-4-chlorophenanthrene, 0.6 g. of cuprous cyanide, a small amount of anhydrous copper sulfate and 1 ml. of dry pyridine were heated together in an open 50-ml. round bottomed flask at 240 ± 20° for five hours.

The black glassy mass which formed on cooling was dissolved in pyridine and the solution was poured into ether. The ethereal solution was extracted with 10% hydrochloric acid, washed with water, dried over anhydrous magnesium sulfate and then evaporated. After treating the residue with ethanol, 0.49 g. (46%) of solid melting at 139–142° was obtained. The analytical sample crystallized from ethanol as pale yellow needles; m.p. 144.5–145°.

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.74. Found: C, 82.20; H, 4.61.

3-Hydroxy-4-cyanophenanthrene (V).—One-tenth gram of 3-methoxy-4-cyanophenanthrene was refluxed for five hours with a solution of 3.3 g. of potassium hydroxide in 10 ml. of ethanol. The reaction mixture was diluted and acidified. The precipitate was dissolved in ether and the ethereal solution in turn was extracted first with 10% sodium bicarbonate and then with 10% sodium hydroxide. Acidification of the first extract yielded almost nothing while acidification of the second with carbon dioxide gave 0.08 g. (85%)

(18) L. F. Fieser, THIS JOURNAL, 51, 940 (1929).

(19) L. F. Fieser, *ibid.*, 51, 1935 (1929).

(20) Aniline attacks 1,2-naphthoquinone at the 4-position; T. Zincke, *Ber.*, 15, 481 (1882).

(21) Tests for activity against *A. niger* were carried out essentially as described by J. M. Leonard, and V. L. Blackford, *J. Bact.*, 57, 339 (1949). The bacteriostatic tests were carried out as described by F. C. Brown, C. K. Bradsher, E. C. Morgan, M. Tetenbaum and P. Wilder, Jr., THIS JOURNAL, 78, 384 (1956).

We are indebted to Mrs. Barbara Bayless for carrying out these tests.

(22) It has been suggested that the decrease in effectiveness of high boiling coal tar acids caused by chlorination may be attributed to diminished solubility; L. P. Curtin and M. T. Bogert, *Ind. Eng. Chem.*, 19, 1231 (1927).

(23) All melting points are corrected. Analyses are by Micro Tech Laboratories.

(24) L. F. Fieser, THIS JOURNAL, 51, 2466 (1929).

(25) A. Werner, *Ann.*, 321, 282 (1902).

(26) J. S. Buck, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 619.

of material melting at 241–243°. On recrystallizing this solid from dilute ethanol, it melted at 245–246°.

Anal. Calcd. for $C_{15}H_9NO$: C, 82.17; H, 4.27. Found: C, 81.96; H, 4.27.

4,9-Dichloro-3-phenanthrol (VIII). (a) By Chlorination of 3-Phenanthrol.—To 15.75 g. (0.081 mole) of 3-phenanthrol in a 125-ml. erlenmeyer flask equipped with a reflux condenser was added 23.4 g. (0.175 mole) of sulfuryl chloride. Evolution of gas began after two minutes and reaction was allowed to continue for ten minutes longer. The resultant mass was recrystallized from glacial acetic acid; yield 15.2 g. (72%) of almost colorless plates of m.p. 141–142°.

(b) By the Chlorination of 4-Chloro-3-phenanthrol.—Two and three-tenths grams (0.01 mole) of 4-chloro-3-phenanthrol was treated directly with 0.8 ml. (0.01 mole) of sulfuryl chloride. After standing for one-half hour the reaction mixture was recrystallized from glacial acetic acid; yield 2.4 g. (91%), m.p. 139–141°. This compound gives no mixture melting point depression with that obtained by procedure (a) above.

Anal. Calcd. for $C_{14}H_8Cl_2O$: C, 63.90; H, 3.06; Cl, 26.95. Found (procedure a): C, 63.95; H, 3.32; Cl, 26.90.

3-Methoxy-4,9-dichlorophenanthrene. (a) By Methylation of 4,9-Dichloro-3-phenanthrol.—One-half gram of 4,9-dichloro-3-phenanthrol was etherified according to the method of Buck.[26] Three-tenths gram (56%) of material of m.p. 81–83° was obtained, and, on recrystallization from absolute ethanol, the expected ether was obtained as colorless needles; m.p. 84–85°.

Anal. Calcd. for $C_{15}H_{10}Cl_2O$: C, 65.00; H, 3.64. Found: C, 65.23; H, 3.74.

(b) By Chlorination of 3-Methoxyphenanthrene.—To 250 mg. (1.2 mmoles) of 3-methoxyphenanthrene in 1 ml. of glacial acetic acid was added 0.326 g. (2.4 mmoles) of sulfuryl chloride. After evaporating the acetic acid under a stream of air, the residual oil was crystallized from absolute ethanol; m.p. 80–82°, yield 0.098 g. (28%). This material did not depress the melting point of that prepared according to procedure (a).

3-Benzoxy-4,9-dichlorophenanthrene.—The benzoate of 4,9-dichloro-3-phenanthrol was prepared by the Schotten–Baumann method using 10% sodium hydroxide. The derivative was obtained as long white needles from glacial acetic acid; m.p. 196.5–197°.

Anal. Calcd. for $C_{21}H_{12}Cl_2O_2$: C, 68.68; H, 3.29. Found: C, 68.55; H, 3.39.

3-Phenanthrol by Reduction of 4-Chloro-3-phenanthrol.—A mixture containing 0.63 g. of 4-chloro-3-phenanthrol, 10 ml. of glacial acetic acid saturated with hydrogen chloride, 0.70 g. of granular tin, 1 ml. of water and 8 ml. of concentrated hydrochloric acid was refluxed for 5 hours, after which the reaction mixture was cooled and diluted to precipitate the product; yield 0.49 g. (91%), m.p. 117–119°. This material gave no mixture melting point depression with an authentic sample of 3-phenanthrol.

9-Chloro-3-phenanthrol (IX).—To 15.2 g. (0.058 mole) of 4,9-dichloro-3-phenanthrol dissolved in 125 ml. of glacial acetic acid was added 8.7 g. (0.074 gram atom) of granular tin; the solution was heated to reflux, and 6 ml. of concentrated hydrochloric acid was added all at once. Also, 2-ml. portions of acid were added hourly to the refluxing solution for 19 hours. After 13 hours an additional 4.4 g. (0.037 gram atom) of tin was added, and at the end of the reaction, when all the tin had dissolved, 12.7 g. (96%) of white solid, m.p. 142–144°, crystallized from the reaction mixture. The product crystallized from chloroform as needles emanating from a central point to form clusters; m.p. 146–147°.

Anal. Calcd. for $C_{14}H_9ClO$: C, 73.53; H, 3.97. Found: C, 73.20; H, 3.94.

3-Methoxy-9-chlorophenanthrene (X).—Methylation of 9-chloro-3-phenanthrol was accomplished according to the etherification technique of Buck.[26] Eleven grams (93%) of white needles of m.p. 73–75° was obtained. An analytical sample was prepared from methanol; m.p. 77.5–78.5°.

Anal. Calcd. for $C_{15}H_{11}ClO$: C, 74.23; H, 4.57; Cl, 14.61. Found: C, 74.12; H, 4.70; Cl, 14.78.

3-Methoxy-9-cyanophenanthrene (XI).—This cyano compound was prepared in essentially the same fashion as was 3-methoxy-4-cyanophenanthrene. From 2.4 g. of 3-methoxy-9-chlorophenanthrene, 1.6 g. (69%) of reaction product of m.p. 109–113° was obtained. On recrystallizing this solid from either ethanol or glacial acetic acid, fine white needles of m.p. 122–122.5° were obtained.

Anal. Calcd. for $C_{16}H_{11}NO$: C, 82.38; H, 4.75. Found: C, 82.08; H, 4.90.

3-Methoxyphenanthrene-9-carboxylic Acid (XII).—After refluxing 0.2 g. of 3-methoxy-9-cyanophenanthrene with a solution composed of 20 ml. of ethanol, 5 ml. of water and 3 g. of sodium hydroxide for seven hours, 0.166 g. (77%) of 3-methoxyphenanthrene-9-carboxylic acid was obtained, m.p. 199–200° (lit.[13] 200°). This material gave no mixture melting point depression with an authentic sample.[27]

Methyl 3-Methoxyphenanthrene-9-carboxylate.—The methyl ester of a small amount of 3-methoxyphenanthrene-9-carboxylic acid was prepared by adding an excess of diazomethane in ether to a benzene solution of the acid. The ester was obtained on partial evaporation of the solvent; m.p. 81–82° (lit.[13] 81.5–82.5°); this material gave no mixture melting point depression with an authentic sample of methyl-3-methoxyphenanthrene-9-carboxylate.[27]

1,2,4,4,9-Pentachloro-3-keto-1,2,3,4-tetrahydrophenanthrene (XIII). (a) By Chlorination of 3-Phenanthrol with Sulfuryl Chloride.—In a 125-ml. erlenmeyer flask equipped with a reflux condenser were placed 9.7 g. (0.05 mole) of 3-phenanthrol, 28.5 g. (0.21 mole) of sulfuryl chloride and 15 ml. of glacial acetic acid. During a two-hour period at room temperature, 6.4 g. (34%) of yellow solid crystallized from the solution; it melted with decomposition at 188–190°.[28] On recrystallization from warm glacial acetic acid, the decomposition point rose to 199–200°.

(b) By Chlorination of 4,9-Dichloro-3-phenanthrol with Sulfuryl Chloride.—Five and four-tenths grams (0.022 mole) of 4,9-dichloro-3-phenanthrol dissolved in 20 ml. of glacial acetic acid was treated at room temperature during a 15 minute reaction period with 6.0 g. (0.044 mole) of sulfuryl chloride. The product (5.7 g., 75%) crystallized from the reaction mixture as ill-formed yellow rods of decomposition point 186–190°. When crystallized, as before, from glacial acetic acid, its decomposition point was raised to 199–200°.

Anal. Calcd. for $C_{14}H_7Cl_5O$: C, 45.63; H, 1.91; Cl, 48.11. Found (Procedure a): C, 46.08; H, 2.27; Cl, 48.22.

(c) By Chlorination of 3-Phenanthrol with Chlorine Gas.—One gram of 3-phenanthrol dissolved in 10 ml. of glacial acetic acid was treated with elemental chlorine according to the directions of Fieser and Dunn.[6] On working the reaction up in the manner described and by triturating the product with glacial acetic acid, material (0.46 g.) melting with decomposition at 176–186° was obtained. Recrystallized from acetic acid, the product appeared as yellow, ill-formed needles melting at 196–198° with decomposition.

As further proof of identity all three preparations (a, b and c) were transformed to 2,4,9-trichlorophenanthrol as described below and the products shown to be identical by mixed melting point determinations.

2,4,9-Trichloro-3-phenanthrol (XV).—Six and three-tenths grams of the 2,2,4,4,9-pentachloro-3-keto-1,2,3,4-tetrahydrophenanthrene, m.p. 188–190°, dissolved in 150 ml. of glacial acetic acid at room temperature was treated with a concentrated solution of stannous chloride in dilute acetic acid until a diluted test portion was completely soluble in 5% sodium hydroxide solution. On diluting the reaction mixture with water there was obtained 5.0 g. (97%) of material melting at 156–159°. From glacial acetic acid, the solid crystallized as white needles, m.p. 165.5–166°.

Anal. Calcd. for $C_{14}H_8Cl_3O$: C, 56.51; H, 2.37; Cl, 35.75. Found: C, 56.43; H, 2.49; Cl, 35.80.

2,4,9-Trichloro-3-acetoxyphenanthrene.—The acetoxy derivative of 2,4,9-trichloro-3-phenanthrol was prepared in essentially quantitative yield by refluxing it for five hours

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(27) We are indebted to Dr. Erich Mosettig for supplying this sample.

(28) A second fraction of crystals, 4.7 g., of less well-defined melting point was obtained from the mother liquor. This material, like the first was insoluble in dilute sodium hydroxide and probably contains isomers including stereoisomers. It was not further investigated.

with an excess of acetic anhydride. The product was crystallized from ethanol as white needles; m.p. 164–165°.

Anal. Calcd. for C₁₆H₉Cl₃O₂: C, 56.58; H, 2.67; Cl, 31.32. Found: C, 56.38; H, 3.08; Cl, 31.38.

2,4,9-Trichloro-3-methoxyphenanthrene.—This methyl ether was prepared from 1.3 g. of the parent hydroxy compound according to the methylation procedure of Buck.[26] Obtained from the reaction mixture was 0.9 g. of material which crystallized as long fluffy needles from ethanol; m.p. 133–134°.

Anal. Calcd. for C₁₅H₉Cl₃O: C, 57.82; H, 2.91; Cl, 34.14. Found: C, 57.74; H, 3.08; Cl, 33.93.

2,4,9-Trichloro-3-benzoxyphenanthrene was prepared from XV by the Schotten–Baumann method. It crystallized as white needles from absolute ethanol; m.p. 173.5–174°.

Anal. Calcd. for C₂₁H₁₁Cl₃O₂: C, 62.79; H, 2.76. Found: C, 63.04; H, 2.91.

2,9-Dichloro-3-phenanthrol (XVI).—One gram of 2,4,9-trichloro-3-phenanthrol, 0.9 g. of granular tin, 25 ml. of glacial acetic acid saturated with hydrogen chloride and 2 ml. of concentrated hydrochloric acid were refluxed together for 46 hours. On cooling and diluting the reaction mixture with water, 0.8 g. (92%) of white solid melting at 145–148° was obtained. From isoöctane, this compound crystallized as small white needles; m.p. 152–153°.

Anal. Calcd. for C₁₄H₈Cl₂O: C, 63.91; H, 3.06; Cl, 26.95. Found: C, 63.87; H, 3.30; Cl, 26.60.

2,9-Dichloro-3,4-phenanthraquinone (XVII). (a) By Oxidation[29] of 2,4,9-Trichloro-3-phenanthrol.—One and seven-tenths grams of 2,4,9-trichloro-3-phenanthrol was dissolved with heating in 60 ml. of glacial acetic acid. The solution was cooled to 27° and 15 ml. of concentrated nitric acid was added all at once. After ten minutes, 10 ml. of water was added dropwise, and the black microcrystalline precipitate was filtered off; weight 1.5 g. (93%), m.p. 228–230° dec. After one recrystallization from glacial acetic acid, the quinone was obtained as small black needles of decomposition point 230° when put in the melting point bath at 200° and heated to the above temperature at the rate of two degrees per minute.

Anal. Calcd. for C₁₄H₆Cl₂O₂: C, 60.68; H, 2.18; Cl, 25.59. Found: C, 60.61; H, 2.48; Cl, 25.87.

(b) **By Oxidation of 2,9-Dichloro-3-phenanthrol.**—To a solution at room temperature composed of 2 ml. of glacial acetic acid and 40 mg. of 2,9-dichloro-3-phenanthrol was added 0.5 ml. of concentrated nitric acid. The solution immediately turned red and precipitated 37 mg. (88%) of black microcrystalline solid; m.p. 228–229°, with decomposition.

When these two products are mixed, the temperature at which the mixture melts and decomposes is not different from that of the individual melting point determinations.

2,9-Dichloro-3,4-diacetoxyphenanthrene.—Two hundred and fifty milligrams of 2,9-dichloro-3,4-phenanthraquinone, 8 ml. of acetic anhydride, 5 ml. of glacial acetic acid, 1 g. of fused sodium acetate and 0.5 g. of zinc dust were stirred together for five minutes. The reaction mixture was filtered and from the colorless filtrate on dilution with water was obtained 240 mg. (74%) of white solid. Crystallized from acetic acid it formed fluffy needles of m.p. 206–207°.

Anal. Calcd. for C₁₈H₁₂Cl₂O₄: C, 59.53; H, 3.33; Cl, 19.53. Found: C, 59.38; H, 3.43; Cl, 19.47.

The 7-Chloronaphtho[2,1-h]quinoxalo[2,3a]phenazine (XXII).—Two hundred milligrams of 2,9-dichloro-3,4-phenanthraquinone in 20 ml. of glacial acetic acid was treated with 0.085 g. of o-phenylenediamine and 1 ml. of concentrated hydrochloric acid in 5 ml. of glacial acetic acid during a two-minute reflux period. Water was added to precipitate the yellow product, weight 0.20 g. After three recrystallizations from pyridine, the solid appeared as small light yellow pellets of indefinite crystalline character melting at 320–321°.

Anal. Calcd. for C₂₆H₁₃ClN₄: C, 74.90; H, 3.14; Cl, 8.50. Found: C, 74.54; H, 3.13; Cl, 8.51.

1,3,4-Triacetoxy-2,9-dichlorophenanthrene (XIX).—Nine-tenths gram of 2,9-dichloro-3,4-phenanthraquinone

was added to 60 ml. of acetic anhydride and 2 ml. of concentrated sulfuric acid was added dropwise to the stirred suspension. Stirring was continued at room temperature for 22 hours during which time a small amount of white solid crystallized from the colorless reaction mixture. This solid (0.131 g., m.p. 205–207°) was filtered from the reaction mixture and the filtrate was poured into 600 ml. of water. The precipitated light orange solid, after one recrystallization from alcohol weighed 1.086 g. and melted at 205–207°. The combined yield was 1.217 g. (89%). Crystallized from a dilute solution in absolute ethanol, the triacetate appeared as wool-like needles, while from more concentrated solutions rectangular plates were obtained. The melting points of the two crystalline modifications were the same: 207–208° with sintering at 190°.

Anal. Calcd. for C₂₀H₁₄Cl₂O₆: C, 57.02; H, 3.35; Cl, 16.84. Found: C, 57.23; H, 3.43; Cl, 16.62.

2,3-Dimethyl-11-chloro-5,6-chrysenequinone (XVIII).—One-half gram of 2,9-dichloro-3,4-phenanthraquinone, 2 ml. of 2,3-dimethylbutadiene and 65 ml. of purified chloroform were placed in a carius tube; the tube was sealed, and heated on the steam-bath for 35 minutes. During this time the quinone dissolved, and the color of the reaction mixture turned gradually to pale yellow. The solvent was evaporated, and the residue. 0.627 g. (97.5%), crystallized poorly. No melting point of the adduct could be obtained since it appeared to decompose into its components and melted at a temperature only slightly below that of the parent quinone. Similar difficulty was encountered in attempting to recrystallize this adduct.

When 100 mg. of the above material was treated at reflux temperature in 5 ml. of absolute ethanol with 100 mg. of fused sodium acetate for five minutes, 47 mg. (49%) of reddish-yellow solid was obtained, m.p. 252–253° (on addition of a solution of silver nitrate to the diluted ethanolic filtrate above, a white precipitate was formed). From glacial acetic acid, the above solid crystallized as red needles with a golden reflex, m.p. 252.5–253°; ultraviolet absorption maxima (and log extinction coefficients) 316 (5.08), 383 (4.82); minima 310 (5.06), and 339 mμ (4.64).

Anal. Calcd. for C₂₀H₁₃ClO₂: C, 74.89; H, 4.07; Cl, 11.05. Found: C, 74.59; H, 4.12; Cl, 11.15.

1,3,4-Triacetoxy-9,10-dihydrophenanthrene.—Five hundred milligrams of 1,3,4-triacetoxy-2,9-dichlorophenanthrene, 500 mg. of fused sodium acetate, 2.5 g. of 10% palladium-on-carbon and 50 ml. of glacial acetic acid were stirred together under a slight pressure of hydrogen for 46 hours. The catalyst was filtered from the reaction mixture; the filtrate was evaporated to a volume of 20 ml. and this concentrated solution was diluted to about 250 ml. with water. After standing at 0° for 22 hours, 263 mg. of white solid was obtained from the diluted reaction mixture. On recrystallization from a benzene–ligroin solution, this material weighed 229 mg. (78%) and melted at 132–134°. The melting point of the analytical sample was 136–137°; ultraviolet absorption maximum (and log extinction coefficient) 266 (4.22); minimum 241 mμ (3.70).

Anal. Calcd. for C₂₀H₁₈O₆: C, 67.79; H, 5.12. Found: C, 67.92; H, 5.14.

3-Hydroxy-1,4-phenanthraquinone (XXI).—To 46 mg. of 1,3,4-triacetoxy-9,10-dihydrophenanthrene in 4 ml. of ethanol was added a solution of one-tenth gram of potassium hydroxide in 2 ml. of water and 4 ml. of ethanol. The reaction mixture was heated to reflux and air was bubbled through it. The solution was first yellow, but after only one minute it became of a wine color. The potassium salt of the hydroxyquinone precipitated and was redissolved by adding 10 ml. of water. The quinone was precipitated by acidifying its basic solution. An orange-yellow solid (26 mg.) crystallized from ethanol as needles emanating from a central point like spokes of a wheel; m.p. 201° with decomposition.[30]

Anal. Calcd. for C₁₄H₈O₃: C, 74.99; H, 3.60. Found: C, 74.43; H, 3.77.

(30) Fieser (ref. 18) observed that this compound sintered at 200° and melted with some decomposition at 230°. Our lower melting point may be due to the more rapid decomposition sometimes seen when compounds are melted on the Fisher–Johns block or, as indicated by the analysis, the presence of a small amount of an impurity. In any event reductive acetylation gave the expected product.

(29) The procedure is essentially that used by Fieser and Dunn (ref. 6) for oxidation of their isomeric trichlorophenanthrol.

1,3,4-Triacetoxyphenanthrene (XX).—Two milligrams of 3-hydroxy-1,4-phenanthraquinone was acetylated in one milliliter of acetic anhydride in the presence of a small amount of fused sodium acetate and zinc dust. After 10 minutes at room temperature, the zinc was filtered from the now colorless solution, and after almost complete evaporation of the solvent, dilute acetic acid was added to the warm residual solution. On dilution and further cooling the product precipitated as a white solid; weight 2 mg., m.p. 134–136°. This compound recrystallized, melted at 137–138° and gave no mixture melting point depression with an authentic sample of 1,3,4-triacetoxyphenanthrene (m.p. 137–138°) obtained from Professor L. F. Fieser.[19]

DURHAM, N. C.

The Synthesis of Tropone and Tropolone *via* a Norcarenone → Cycloheptadienone Rearrangement

BY EUGENE E. VAN TAMELEN AND GEORGE T. HILDAHL[1]

The *p*-toluenesulfonate of 5-hydroxymethyl-2-cyclohexenone, the synthesis of which is described, yields 2,4-cycloheptadienone on treatment with alkali. The latter ketone can be oxidized through a variety of techniques to tropone; or, as the enol acetate, it can be transformed to tropolone on oxidation with peracids.

At the time this research was initiated there had been described two routes to that unusual aromatic prototype, *tropone* (cycloheptatrienylium

Ia   Ib
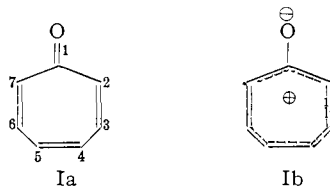
oxide) (Ia or Ib), namely, those described by (1) Dauben and Ringold,[2] who catalytically hydrogenolyzed 2,4,7-tribromotropone, which resulted from the bromination and subsequent heating of 2-cycloheptenone and (2) Doering and Detert,[3] who brominated the product ("methoxytropilidene") obtained by irradiating a mixture of anisole and diazomethane.[4] Because of tropone's novel position in the field of aromatic chemistry and because of the occurrence of the closely related *tropolone* (II) system in various natural products, we believed it worthwhile to attempt the de-

II
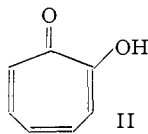
velopment of new synthesis routes promising adaptability, selectivity and general usefulness. With this purpose in mind we have undertaken two distinct approaches: one involving facile, simple elimination from a seven-membered carbocyclic system with the *direct* formation of the troponoid structure[5]; and a second, featuring the

preparation of a well-defined, key *intermediate* which, approaching as closely as possible in oxidation state the tropone (or tropolone) molecule, should be transformable to the desired system through mild dehydrogenation or oxidation techniques. The present account is concerned with the second approach and is divided into three parts: the synthesis of *2,4-cycloheptadienone* (III), the conversion of III to tropone, and the preparation of tropolone from III.

III
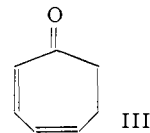
Synthesis of 2,4-Cycloheptadienone.—Eucarvone (IV) is an authentic 2,4-cycloheptadienone which

IV
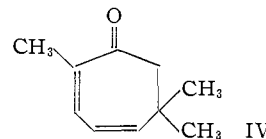
was prepared many years ago by Baeyer[6] and, as demonstrated by Wallach,[7] evolves by a rather unusual route: the ring enlargement which accompanies the ready dehydrohalogenation of carvone hydrobromide (V) by alkali. This transfor-

V
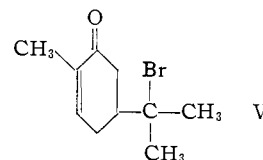
mation gained the attention of Lapworth,[8] who supported Wallach's suggestion[7] that it proceeded by way of carenone (VI), which substance, however, could not be isolated and, even now, remains unknown. Nevertheless, the route involving initial ring closure to VI is eminently reasonable[9]; and

(1) Summer Research Assistant 1953 and 1955. Part of this work was first presented in a Communication to the Editor, THIS JOURNAL, **75**, 5451 (1953).

(2) H. J. Dauben, Jr., and H. J. Ringold, *ibid.*, **73**, 876 (1951).

(3) W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).

(4) Subsequently we learned that T. Nozoe, Y. Kitahara, T. Ando and S. Masamune (*Proc. Japan Acad.*, **27**, 415 (1951); *C.A.*, **46**, 7558 (1952)) reported the successful application of the brominative dehydrogenation technique to cycloheptanone itself, the major product being 2,4,7-tribromotropone (ref. 2).

(5) Unpublished results obtained in this Laboratory by Miss P. Barth.

(6) A. Baeyer, *Ber.*, **27**, 810 (1894).

(7) O. Wallach and H. Kohler, *Ann.*, **339**, 94 (1905).

(8) R. W. L. Clarke and A. Lapworth, *J. Chem. Soc.*, **97**, 11 (1910).

(9) N. D. Zelinsky and E. F. Dengin, *Ber.*, **55B**, 3354 (1922).