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

Studies in the Phenanthrene Series. XXIII. Synthesis of Acyl Compounds Derived from 2-Hydroxy-9,10-dihydrophenanthrene[1]

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This investigation was undertaken with the aim of synthesizing compounds from which, because of their structural similarity to oestrone (I), some oestrogenic activity might be expected.[2] 2-Hydroxy-9,10-dihydrophenanthrene (II) appeared particularly suited to building up compounds of the desired type, first because its phenolic hydroxyl group is located in a position corresponding to that of the phenolic hydroxyl in oestrone, and second, we anticipated that in the Friedel–Crafts reaction or the Fries rearrangement with 2-hydroxy(or acetoxy-)-9,10-dihydrophenanthrene the acyl group would enter chiefly position 7, which, again, corresponds to the position of the carbonyl in the hormone. Such speculation seemed justified by our experience with 9,10-dihydrophenanthrene, which, in respect to monosubstitution, behaves like diphenyl rather than like phenanthrene, acyl groups,[3] the nitro group[4] and the sulfonic group entering solely or chiefly position 2, which corresponds to position 4 in diphenyl. It has been shown recently by Fieser and Bradsher[5] and by Cheetham and Hey[6] that

the alkoxyl and hydroxyl group in position 4 of diphenyl directs acyl groups to positions 4' and 3, which corresponds to position 7 and position 3 or 1 of 9,10-dihydrophenanthrene.

It appeared desirable to find a more convenient method for the large scale preparation of the starting material, 2-hydroxy-9,10-dihydrophenanthrene, than that described previously[3c] (Beckmann rearrangement of the oxime of the acetyl derivative, and subsequent diazotization of the amine). The customary method of sulfonation, followed by potassium hydroxide fusion, failed in this instance. Although dihydrophenanthrene gave under certain conditions the 2-sulfonic acid in a yield of 50–60%, in the potassium hydroxide fusion dehydrogenation took place simultaneously, yielding 2-hydroxyphenanthrene. Nevertheless it is worthy of note that by this series of reactions phenanthrene can be converted to 2-hydroxyphenanthrene in an over-all yield of from 20 to 25%, and it is likely that this yield can be improved by systematic experimentation. In the meantime a convenient method for the preparation of 2-amino-9,10-dihydrophenanthrene, via the nitro compound, was worked out in this Laboratory.[4] From this amine the desired 2-hydroxy-9,10-dihydrophenanthrene was obtained in a yield of 69% when the diazotization was carried out according to de Milt and van Zandt.[7]

(1) Paper XXII, THIS JOURNAL, **60**, 2962 (1938).

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(2) See also the previous papers XIV and XVIII of this series. (a) Mosettig and Duvall, THIS JOURNAL, **59**, 367 (1937); (b) Duvall and Mosettig, ibid., **60**, 2409 (1938).

(3) (a) Burger and Mosettig, ibid., **57**, 2731 (1935); (b) ibid., **58**, 1857 (1936); (c) ibid., **59**, 1302 (1937).

(4) A by-product in the nitration is 4-nitro-9,10-dihydrophenanthrene. Krueger and Mosettig, Studies in the Phenanthrene Series. XX, J. Org. Chem., in press.
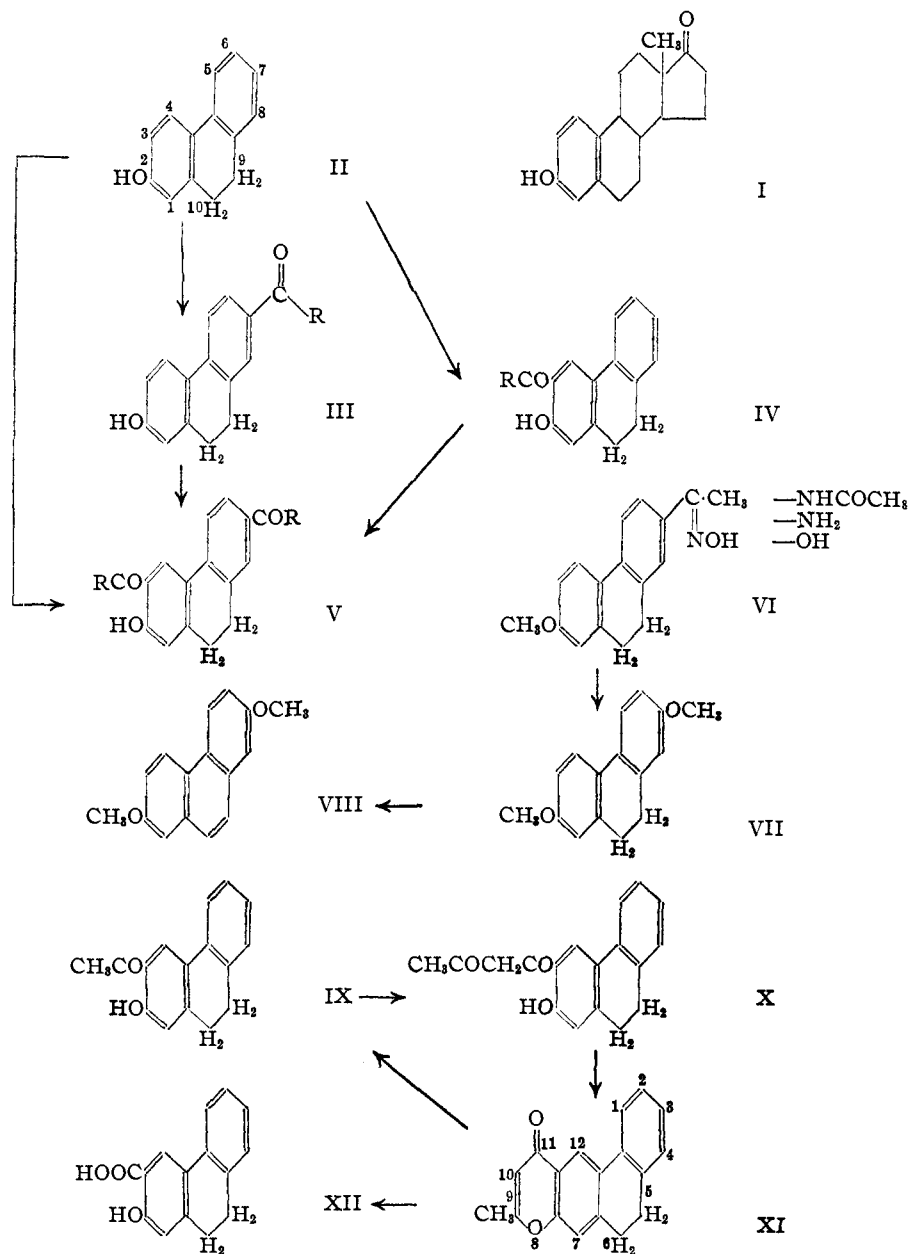
(5) Fieser and Bradsher, THIS JOURNAL, **58**, 1738, 2337 (1936).

(6) Cheetham and Hey, J. Chem. Soc., 770 (1937). See also Hey and Jackson, ibid., 802 (1936).

(7) De Milt and van Zandt, THIS JOURNAL, **58**, 2044 (1936). See also Bachmann and Boatner, ibid., **58**, 2194 (1936).

In the Friedel–Crafts reaction with 2-hydroxy-9,10-dihydrophenanthrene, employing two molecular equivalents of acetyl chloride, and nitrobenzene as solvent, two acyl derivatives were obtained. The major product (60–65%) was the expected 2-hydroxy-7-acetyl-9,10-dihydrophenanthrene (III, R = CH₃). The by-product (15–20%) resulted from disubstitution and was shown to be 2-hydroxy-3,7-diacetyl-9,10-dihydrophenanthrene (V, R = CH₃). The reaction of 2-acetoxy-9,10-dihydrophenanthrene with one molecular equivalent of acetyl chloride gave, under similar

conditions, practically the same results. When, however, the free hydroxy compound was allowed to react with only one molecular equivalent of acetyl chloride, the only product that could be isolated from the reaction mixture (in a yield of approximately 20%) was the ortho substituted 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene (IV, R = CH₃). This compound reacted readily with an excess of acetyl chloride (nitrobenzene, AlCl₃) to give the hydroxydiacetyl derivative (V, R = CH₃) and may be, therefore, an intermediate in the formation of V. The 7-acetyl derivative

III (R = CH₃) can also be converted to the di-acetyl compound V, but only in such low yields as to suggest that it is not the precursor of the latter.

The Fries rearrangement proved to be some-what less satisfactory for the production of acyl compounds. It was best carried out, according to the method of Fieser and Bradsher,[5] by heating an equimolecular mixture of 2-acetoxy-9,10-dihy-drophenanthrene and aluminum chloride at 140°. From this reaction the isomeric monoacetyl de-rivatives III and IV (R = CH₃) were formed in about equal amounts and were readily separated by the difference in their solubilities. In analogy to the diphenyl series, the 7-acetyl isomer III—corresponding to the 4,4'-diphenyl derivative—is higher melting and less soluble than the 3-acetyl derivative IV—corresponding to the 4,3-diphenyl derivative. For unknown reasons the yields could not always be duplicated.

The reaction of 2-methoxy-9,10-dihydrophe-nanthrene with one mole of acetyl chloride, under the usual conditions, proceeded smoothly, and a mixture apparently of 2-methoxy-7-acetyl- and 2-methoxy-3-acetyl-9,10-dihydrophenanthrene was obtained in good yields. We were unable to ef-fect separation of the mixture, and its constituents were identified only after hydrolysis of the meth-oxyl group by the action of hydrobromic acid, a procedure that destroyed most of the material.

The higher acyl homologs of 2-hydroxy-7-acetyl-9,10-dihydrophenanthrene were prepared by the Friedel–Crafts reaction using two molecu-lar equivalents of propionyl and butyryl chloride, respectively. The relative extent of disubstitu-tion increased with increasing molecular weight of the acyl chloride used, as shown below.

Acid chloride	Yield of III, %	Yield of V, %
Acetyl-	60–65	15–20
Propionyl-	40	35–40
n-Butyryl-	30	50

The relative insolubility of the colorless, higher-melting 7-acyl derivatives in benzene simplified separation from the yellow diacyl compounds which are very soluble in this medium.

In order to prove that the acyl groups in each of the monoacyl derivatives III (R = –CH₃, –C₂H₅, –n-C₃H₇) and in each of the diacyl derivatives V (R = –CH₃, –C₂H₅, –n-C₃H₇) occupy the same relative positions, namely, position 7 and posi-tions 3, 7, respectively, the individual hydroxy-acyl derivatives in question were methylated and

subsequently oxidized with sodium hypochlorite. Each of the hydroxy monoacyl derivatives (III) gave 2-methoxy-9,10-dihydrophenanthrene-7-car-boxylic acid, and likewise all the hydroxy diacyl derivatives (V) gave 2-methoxy-9,10-dihydro-phenanthrene-3,7-dicarboxylic acid. The loca-tion of the acyl group of the monoacyl derivatives III in position 7 appears to be established by con-version of the oxime (VI) of 2-methoxymonoacetyl dihydrophenanthrene, through the Beckmann rearrangement and subsequent hydrolysis, to a methoxyamino compound, which by diazotization followed by methylation, gave a dimethoxy-9,10-dihydrophenanthrene (VII). This product was finally dehydrogenated to a dimethoxyphenan-threne VIII, which proved to be identical (melt-ing point and mixture melting point) with an au-thentic sample of 2,7-dimethoxyphenanthrene synthesized by Professor Fieser.[8]

As to the structure of the isomeric 2-hydroxy-monoacetyl derivative IV (R = CH₃), the acetyl group was expected, in analogy to the substitu-tion regularities in the diphenyl series,[5,6] to oc-cupy a position ortho to the phenolic hydroxyl. In order to prove this point, the hydroxy acetyl derivative IX was converted via the β-diketone X to the chromone derivative XI, by following essen-tially the preparative procedure applied by Cheet-ham and Hey[6,9] to the analogous 4-hydroxy-3-acetyldiphenyl. As is characteristic of chro-mones, the chromone derivative XI gave, on treatment with hot alkali, chiefly the hydroxy acid XII, while 2-hydroxy-3-acetyl-9,10-dihydro-phenanthrene (IX) was formed as a by-product.

By oxidation of the methyl ether of IX with sodium hypochlorite, a carboxylic acid was ob-tained, whose methyl ester gave on palladium de-hydrogenation a methyl ester of m. p. 94–95° (m. p. of acid 213–214°), which was obviously different from 2-methoxyphenanthrene-1-carbox-ylic acid methyl ester of m. p. 145–146° (m. p. of acid 244–246°).[10] Thereby position 1 for the lo-cation of the acyl group in IX (IV) was excluded, and for this isomeric hydroxyacetyl compound, therefore, only the structure of a 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene remains open.

The structure of the diacetyl derivative V (R = CH₃), and its homologs, follows from the synthesis of V (R = CH₃) from each of the isomeric mono-

(8) See Fieser, THIS JOURNAL, **51**, 2481 (1929).
(9) For further references see Heilbron, Hey and Lowe. *J. Chem. Soc.*, 1311 (1934).
(10) Mosettig and Burger, THIS JOURNAL, **55**, 2981 (1933).

acyl compounds III and IV (R = CH₃) by the Friedel–Crafts reaction.

The similarity of 9,10-dihydrophenanthrene derivatives and diphenyl derivatives, with respect to the regularities of substitution, melting points and solubilities is rather complete save for the fact that no disubstitution has been observed in the Friedel–Crafts reaction on 4-hydroxydiphenyl. Furthermore, it should be noted that ortho substitution (in the Friedel–Crafts reaction and the Fries rearrangement) in 2-hydroxy-, 2-acetoxy- and 2-methoxy-9,10-dihydrophenanthrene takes place in position 3. The ortho substitution observed in the analogous reactions on 2-hydroxy-, 2-acetoxy- and 2-methoxyphenanthrene took place apparently only in position 1.[10,11] These results recall previously made observations on ring closures of the side chains —C—C—C, —C—C—C— C— and —N—C—C—C— attached to position 2 of 9,10-dihydrophenanthrene and phenanthrene, respectively. The cyclization of the dihydrophenanthrene derivatives takes place chiefly or entirely in position 3, while the cyclization of the phenanthrene derivatives takes place in position 1.[12]

Seven of the compounds described in this communication, namely, 2-hydroxy-, 2-hydroxy-7-acetyl, 2-acetoxy-7-acetyl-, 2-hydroxy-7-propionyl-, 2-hydroxy-7-butyryl-, 2-hydroxy-3,7-dipropionyl-, 2-hydroxy-3,7-dibutyryl-9,10-dihydrophenanthrene were tested for oestrogenic activity at the Squibb Institute for Medical Research (Dr. Geo. A. Harrop, Director). As reported by Mr. Holaday, the samples were injected subcutaneously in corn oil, or 95% alcohol, according to solubility, and total doses up to 100 mg. of sample per rat were administered. The samples failed to produce any sign of oestrus with the single exception of 2-acetoxy-7-acetyl-9,10-dihydrophenanthrene, which exhibited in doses of 75 or 100 mg. a definite but very slight oestrogenic activity.[13]

(11) Since the yields were generally poor and no complete separation of the various reaction mixtures could be effected at that time we refrain from definite conclusions. Incidentally, the present investigation eliminates positions 3 and 7 for *x* in the previously described 2-acetoxy-*x*-acetylphenanthrene as can be seen by comparison of the melting points of the corresponding derivatives of 2-methoxyphenanthrene-*x*-carboxylic acid (m. p. 251–252°, methyl ester, m. p. 79–80°) and of 2-methoxyphenanthrene-3-carboxylic acid (m. p. 213–214°, methyl ester, m. p. 94–95°) and of 2-methoxyphenanthrene-7-carboxylic acid methyl ester (m. p. 135°).

(12) For literature references see Mosettig and Krueger, Studies in the Phenanthrene Series, XIX, *J. Org. Chem.*, in press.

(13) None of the phenanthrene derivatives described in the previous paper[2b] namely 1-hydroxy-2-acetyl-, 1-hydroxy-2-propionyl-, 4-hydroxydiacetyl-, 4-hydroxydipropionyl-, 4-hydroxy-*y*-acetyl-, 4-methoxy-*x*-acetyl-, and 4-methoxy-*x*-propionyl-phenanthrene showed any oestrogenic activity.

We are indebted to Professor Fieser for furnishing us with a sample of 2,7-dimethoxyphenanthrene for the purpose of identification.

Experimental

Sulfonation of 9,10-Dihydrophenanthrene.—Schroeter and co-workers[14] have reported a mixture of disulfonic acids from treatment of dihydrophenanthrene with a large excess of concentrated sulfuric acid at 80°. We find that stirring dihydrophenanthrene with two molecular equivalents of c. p. sulfuric acid for four to five hours at 40° results chiefly in monosulfonation. After dilution the sulfonic acid was precipitated as the sodium salt with sodium hydroxide, purified through its difficultly soluble barium salt and isolated as sodium salt; yield 50–60%. Its sulfochloride melts at 137°.

Anal. Calcd. for C₁₄H₁₁O₂SCl: Cl, 12.72. Found: Cl, 12.81.

From the mother liquors a small amount of a sulfonic acid (possibly a disulfonic acid) was isolated which gave a sulfochloride of m. p. 240–242°.

Sulfonation with chlorosulfonic acid in carbon tetrachloride below 10° gave similar results, the yield of monosulfonic acid being somewhat lower. Potassium hydroxide fusion of the sodium salt of dihydrophenanthrene sulfonic acid at 300° gave as sole product 2-hydroxyphenanthrene. After purification by sublimation and crystallization from benzene–petroleum ether, it melted at 166–167°. The mixture melting point with an authentic sample of 2-hydroxyphenanthrene showed no depression; yield 50%.

2 - Hydroxy - 9,10 - dihydrophenanthrene.—2 - Amino-9,10-dihydrophenanthrene was prepared by reduction of the corresponding nitro compound, which was obtained as the main product in the nitration of 9,10-dihydrophenanthrene.[4] The diazotization was carried out conveniently in relatively small runs, of which the following is typical: nitrosylsulfuric acid was prepared by adding 19.5 g. of sodium nitrite in small portions to a stirred, ice-cold mixture of 195 cc. of c. p. sulfuric acid and 98 cc. of water, and warming the mixture on the water-bath to about 40° until a clear solution resulted. To this well-stirred solution, which was cooled with ice and salt to 0°, was added a solution of 25.4 g. of the amine in 130 cc. of pyridine in the course of two hours, the temperature of the reaction mixture being maintained at 0° (±2°). The mixture was stirred for an additional hour and then diluted with ice and water to a volume of about 2500 cc. An aqueous solution of 13 g. of urea was added and stirring was continued for another hour at 0°. The cold solution of the diazonium salt was then filtered rapidly from the orange scum which had formed, and poured into 5 liters of boiling water. Boiling was continued for about one-half hour. When the solution cooled, the reaction product settled as a partly tarry, brown solid, which could be filtered off. The desired phenol was extracted from the precipitate with dilute (1–2%) potassium hydroxide solution. It was purified by distillation at 2 mm. and by crystallization from benzene–petroleum ether and melted at 111–113°; average yield 69%, over-all yield from dihydrophenanthrene 26%.

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

Friedel–Crafts Reactions (a).—An ice-cold solution of 2.1 moles of aluminum chloride in dry nitrobenzene (3 cc. per gram of aluminum chloride) was added slowly at 0° to a solution of one mole of 2-hydroxy-9,10-dihydrophenanthrene and 2.1 moles of acid chloride (acetyl, propionyl or butyryl chloride) in the minimum amount of nitrobenzene (approximately 2.5 cc. per gram of phenanthrene derivative). The mixture was allowed to stand at about 5° for seventy-two hours and then decomposed and worked up in the usual manner. The crude reaction products were saponified by warming with dilute methanolic potassium hydroxide solution. After further dilution with water, and acidification, the oily mixture of crude hydroxy-acyldihydrophenanthrene derivatives that precipitated was dried in a desiccator and dissolved in the minimum amount of boiling benzene. On cooling and standing for several hours, most of the 7-acyl derivative (III) crystallized out. By successive concentration and cooling of the filtrate, all of this derivative could be separated. It was purified by recrystallization from benzene, by sublimation and by final crystallization from ethanol. The 3,7-diacyl derivative (V) formed in this reaction would not crystallize from benzene, but remained as an oil after all of this solvent had been removed. It crystallized when triturated with ethanol and was purified by crystallization from this solvent.

(b).—The reaction of 2-acetoxy-9,10-dihydrophenanthrene with one equivalent of acetyl chloride gave results that were identical with those obtained when two equivalents of acetyl chloride and one equivalent of the 2-hydroxy derivative were allowed to react.

(c).—The reaction of 1.0 g. of 2-hydroxy-9,10-dihydrophenanthrene with 0.37 cc. (one mole) of acetyl chloride under the above conditions gave tarry products from which, as the only crystalline substance, 0.2 g. of 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene (IV) was isolated.

(d).—The reaction of 2-methoxy-9,10-dihydrophenanthrene with one equivalent of acetyl chloride (twenty-one hours reaction time) produced in a yield of about 70% a white crystalline mixture of acyl compounds which could not be separated. Refluxing the mixture with a 15% hydrogen bromide solution in glacial acetic acid brought about much decomposition, but from the resulting tar very small amounts of 2-hydroxy-3-acetyl- and 2-hydroxy-7-acetyl-9,10-dihydrophenanthrene could be isolated.

(e).—A mixture of 0.5 g. of 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene, 0.4 cc. of acetyl chloride and 0.75 g. of aluminum chloride in 5 cc. of nitrobenzene was allowed to stand at 5° for ninety hours. A yield of 0.35 g. of 2-hydroxy-3,7-diacetyl-9,10-dihydrophenanthrene was obtained.

A mixture of 1.0 g. of 2-hydroxy-7-acetyl-9,10-dihydrophenanthrene, 0.8 cc. of acetyl chloride and 1.5 g. of aluminum chloride in 10 cc. of nitrobenzene was allowed to stand at 5° for seventy-two hours. In working up the reaction product, 0.85 g. of unchanged starting material was recovered, and only 0.05 g. of 2-hydroxy-3,7-diacetyl-9,10-dihydrophenanthrene could be isolated. (A careful investigation of the original starting material failed to show the presence of any trace of the diacetyl compound.) The identity of the diacetylhydroxy compound obtained in the above reactions with that obtained from 2-hydroxy(or acetoxy)-9,10-dihydrophenanthrene was established by mixture melting points.

Fries Rearrangement.—When a mixture of 2-acetoxy-9,10-dihydrophenanthrene and aluminum chloride in nitrobenzene was allowed to stand at low temperature (5°) for eighty hours, no reaction took place. When the reaction mixture was kept at room temperature for seventy-two hours or at 140° for one-half hour, 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene (IV) could be isolated in a yield of about 20% from the crude tarry reaction products. The rearrangement, however, gave the most satisfactory results when carried out according to Fieser and Bradsher.[5] One gram of the 2-acetoxy compound was mixed with 0.7 g. of aluminum chloride and 5 cc. of carbon disulfide. The latter was evaporated and the residue was heated at 140° for thirty minutes. After decomposition with water and saponification with alkali the hydroxyacyl compounds were separated by their differing solubility in benzene, the 7-acetyl isomer III (R = CH$_3$) being less soluble than the 3-acetyl isomer IV (R = CH$_3$). The average yields from five 1-g. runs were 23% of III and 24% of IV.

Methylation.—The phenolic hydroxyl in each of the compounds listed was smoothly and quantitatively methylated[15] by adding dimethyl sulfate dropwise, with vigorous stirring, to a suspension of the respective compound in acetone and 66% potassium hydroxide (by weight, one part of hydroxy compound and 2.8 parts of potassium hydroxide; by volume, 1.45 parts of water, 10 parts of acetone and 1.6 parts of dimethyl sulfate).

Acetylations.—The hydroxy compound was refluxed for four to six hours with ten times its weight of acetic anhydride and one-fifth of its weight of anhydrous sodium acetate.

Oxidation.—Each of the methoxyacyldihydrophenanthrenes was oxidized to the corresponding carboxylic acid in the customary way, by refluxing it with a 1% solution of sodium hypochlorite containing a little sodium hydroxide, until a clear solution resulted. The acids were esterified by means of diazomethane. The identity of the acids obtained from the homologous acyl derivatives was established by melting point and mixture melting point determination of both acid and methyl ester.

Dehydrogenation.—Each of the methoxydihydrophenanthrene-carboxylic acid methyl esters (0.2–0.3 g.) was mixed with 10–20% of its weight of palladinized charcoal (containing 17% of palladium) and heated in a small glass bulb, the initial temperature of 200° being raised to 300° in the course of fifteen minutes. The reaction mass was cooled, broken up and extracted with ether. The dehydrogenation products, the methoxyphenanthrene-carboxylic acid methyl esters, were purified finally by sublimation in an oil-pump vacuum, or crystallization from methanol and subsequent sublimation. The average yield was somewhat better than 50%.

Oxime of 2-Methoxy-7-acetyl-9,10-dihydrophenanthrene.—This oxime was prepared, following the directions of Meisenheimer[16] and co-workers for a similar oxime

(15) Stevens and Tucker, *J. Chem. Soc.*, **123**, 2140 (1923).

(16) Meisenheimer, Theilacker and Beisswenger, *Ann.*, **495**, 273 (1932).

TABLE I

DERIVATIVES OF 9,10-DIHYDROPHENANTHRENE

Substituents	Appearance	Solvent	Yield, %	M. p., °C.	Formula	Analyses C, % Calcd.	Found	H, % Calcd.	Found
2-Methoxy-	White	MeOH	Quant.	55	$C_{15}H_{14}O$	85.67	85.68	6.72	6.73
2-Acetoxy-	White	85% EtOH	Quant.	64–65	$C_{16}H_{14}O_2$	80.65	80.74	5.93	5.89
2-Hydroxy-7-acetyl-	White lozenges	Benzene or EtOH	60–65	190	$C_{16}H_{14}O_2$	80.65	80.62	5.93	5.75
2-Methoxy-7-acetyl-	White	MeOH	Quant.	134	$C_{17}H_{16}O_2$	80.92	81.02	6.39	6.24
2-Acetoxy-7-acetyl-	White	EtOH	Quant.	99	$C_{18}H_{16}O_3$	77.12	77.39	5.75	5.75
2-Hydroxy-3-acetyl-	Pale yellow needles	EtOH	24	101	$C_{16}H_{14}O_2$	80.65	80.79	5.93	5.83
2-Methoxy-3-acetyl-	White	MeOH	Quant.	102	$C_{17}H_{16}O_2$	80.92	80.98	6.39	6.24
2-Hydroxy-7-propionyl-	White	Benzene or EtOH	40	197–198	$C_{17}H_{16}O_2$	80.92	80.97	6.39	6.24
2-Methoxy-7-propionyl-	White	MeOH	Quant.	125	$C_{18}H_{18}O_2$	81.17	81.20	6.81	6.81
2-Hydroxy-7-butyryl-	White	Benzene or EtOH	30	176	$C_{18}H_{18}O_2$	81.17	81.22	6.81	6.80
2-Methoxy-7-butyryl-	White	MeOH	Quant.	61.5	$C_{19}H_{20}O_2$	81.40	81.34	7.19	6.89
2-Hydroxy-3,7-diacetyl-	Pale yellow needles	EtOH	15–20	155	$C_{18}H_{16}O_3$	77.12	77.47	5.75	5.52
2-Methoxy-3,7-diacetyl-	White	MeOH	Quant.	167–168	$C_{19}H_{18}O_3$	77.56	77.26	6.16	5.98
2-Hydroxy-3,7-dipropionyl-	Pale yellow needles	EtOH	35–40	129–130	$C_{20}H_{20}O_3$	77.90	78.17	6.54	6.63
2-Methoxy-3,7-dipropionyl-	White	MeOH	Quant.	157	$C_{21}H_{22}O_3$	78.23	78.94	6.88	6.93
2-Hydroxy-3,7-dibutyryl-	Pale yellow needles	EtOH	50	93–94	$C_{22}H_{24}O_3$	78.54	78.88	7.19	7.27
2-Methoxy-3,7-dibutyryl-	White	MeOH	Quant.	102	$C_{23}H_{26}O_3$	78.82	79.22	7.48	7.31

TABLE II

DERIVATIVES OF 9,10-DIHYDROPHENANTHRENE

Substituents	Appearance	Solvent	Yield, %	M. p., °C.	Formula	Analyses C, % Calcd.	Found	H, % Calcd.	Found
2-Methoxy-7-carboxylic acid	White needles	Toluene	90	210	$C_{16}H_{14}O_3$	75.57	76.04	5.55	5.87
Methyl ester	White	MeOH	Quant.	85.5	$C_{17}H_{16}O_3$	76.10	76.26	6.01	6.32
2-Methoxy-3-carboxylic acid	White needles	Benzene–pet. ether	90	163–164	$C_{16}H_{14}O_3$	75.57	76.02	5.55	5.93
Methyl ester	White needles	MeOH	Quant.	80–81	$C_{17}H_{16}O_3$	76.10	76.81	6.01	6.27
2-Methoxy-3,7-dicarboxylic acid	White	EtOH	75	308–309	$C_{17}H_{14}O_5$	68.45	68.25	4.73	4.75
Methyl ester	White	MeOH	90	119	$C_{19}H_{18}O_5$	69.93	69.99	5.56	5.72

TABLE III

DERIVATIVES OF PHENANTHRENE

Substituents	Appearance	Solvent	M. p., °C.	Formula	Analyses C, % Calcd.	Found	H, % Calcd.	Found
2-Methoxy-3-carboxylic acid	White needles	Benzene	213–214	$C_{16}H_{12}O_3$	76.17	76.46	4.80	4.81
Methyl ester	White	Dilute MeOH	94–95	$C_{17}H_{14}O_3$	76.67	76.60	5.30	4.95
2-Methoxy-7-carboxylic acid methyl ester	White	MeOH	135	$C_{17}H_{14}O_3$	76.67	76.69	5.30	5.30
2-Methoxy-3,7-dicarboxylic acid	White	EtOH	320–321 (dec.)	$C_{17}H_{12}O_5$	68.91	69.36	4.08	4.29
Methyl ester	White	MeOH	161–162	$C_{19}H_{16}O_5$	70.36	70.03	4.97	4.55

preparation, by refluxing a saturated solution of the ketone in methanol with 2 moles of hydroxylamine hydrochloride and 2.5 moles of anhydrous sodium acetate. Only one of the possible isomeric forms was obtained. It crystallized from methanol in little white plates, m. p. 161°, yield nearly quantitative.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41; N, 5.24. Found: C, 77.07; H, 6.57; N, 5.22.

2 - Methoxy - 7 - acetylamino - 9,10 - dihydrophenanthrene.—The oxime was dissolved in a mixture of equal amounts of acetic acid and acetic anhydride, the solution was saturated with dry hydrogen chloride and the resulting pasty mass was allowed to stand overnight. The acetylamino compound, obtained by dilution with water, was recrystallized from methanol; m. p. 176.5°.

Anal. Calcd. for $C_{17}H_{17}O_2N$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.49; H, 6.58; N, 5.49.

2 - Methoxy - 7 - amino - 9,10 - dihydrophenanthrene.—The acetylamino compound was hydrolyzed by refluxing it (1 part) with a mixture of glacial acetic acid (6 parts) and 6 N hydrochloric acid (6 parts) for one hour. The amine hydrochloride separated from the boiling solution and was filtered off after cooling. The free base obtained from the hydrochloride with ammonia was sublimed in an oil-pump

vacuum and recrystallized from absolute ethanol; m. p. 146°.

Anal. Calcd. for $C_{15}H_{15}ON$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.75; H, 6.77; N, 6.39.

2,7-Dimethoxy-9,10-dihydrophenanthrene.—A solution of 1.1 g. of the above described amine in 5 cc. of pyridine was added in the course of one hour to an ice-cold solution of nitrosylsulfuric acid, prepared as described above by dissolving 0.8 g. of sodium nitrite in 8 cc. of sulfuric acid and 4 cc. of water. The mixture was stirred for one hour and diluted with water to a volume of 100 cc. One-half gram of urea was added and stirring was continued for one hour longer. The resulting filtered solution was then poured into 400 cc. of boiling water. After cooling, the phenolic product was separated from tarry by-products by alkali extraction and methylated with dimethyl sulfate. The crude dimethoxy compound (0.7 g.) was purified by crystallization from methanol; m. p. 112°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.14; H, 6.65.

A mixture of 0.2 g. of the dimethoxy-9,10-dihydrophenanthrene and 0.05 g. of palladinized charcoal was heated at 300° for thirty minutes. The reaction mixture was extracted with ether and the ether residue was crystallized

from methanol and sublimed in an oil-pump vacuum; m. p. 168–169°. The mixture melting point with a sample of Dr. Fieser's[8] 2,7-dimethoxyphenanthrene was at 168–169°.

2 - Hydroxy - 3 - acetoacetyl - 9,10 - dihydrophenanthrene.—A solution of 1.0 g. of 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene in 20 cc. of dry ethyl acetate was added to 0.4 g. of powdered sodium, and the mixture was refluxed for thirty minutes on the water-bath. It was then poured onto 15 g. of ice and a pellet of sodium hydroxide was added. The yellow precipitate, the sodium salt of the diketone, was filtered and dissolved in water. On acidification, 0.9 g. of crude diketone was obtained, which was recrystallized from 70% ethanol. The hot solutions were bright yellow, but the solid was nearly colorless; m. p. 131–132°.

Anal. Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.28; H, 5.74.

9 - Methyl - 5,6 - dihydronaphtho[1,2 - g]chromone.[17]—Ring closure of the above diketone was brought about quantitatively by boiling it for ten to fifteen minutes in glacial acetic acid containing a few drops of concentrated hydrochloric acid. The chromone derivative was precipitated by diluting the reaction mixture with water. It is insoluble in alkali and crystallized from ethanol in white plates of m. p. 198°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.64; H, 5.77.

(17) The orientation, name and numbering of this compound was devised upon the nomenclature principles as given by Patterson, THIS JOURNAL, 50, 3074 (1928). For the numbering of the chromone, the "parent" component, see Decennial Index of Chemical Abstracts, 3423, 1917–1926.

When refluxed with 2 N sodium hydroxide solution, the chromone derivative went gradually into solution in the course of three hours. From the reaction mixture was obtained 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene in a yield of 15% and 2-hydroxy-9,10-dihydrophenanthrene-3-carboxylic acid in a yield of 60%. The latter compound crystallized from benzene in colorless needles of m. p. 219–220°.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.04. Found: C, 75.17; H, 5.14.

Methylation of the hydroxy acid with dimethyl sulfate gave 2-methoxy-9,10-dihydrophenanthrene-3-carboxylic acid methyl ester, which was identified by melting point and mixture melting point with the compound obtained from 2-hydroxy-3-acetyl-9,10-dihydrophenanthrene (Table III).

Summary

In the Friedel–Crafts reaction and the Fries rearrangement with 2-hydroxy- and 2-acetoxy-9,10-dihydrophenanthrene, respectively, the aliphatic acyl group enters position 3 and position 7. Depending upon the experimental conditions, 2-hydroxy-3-acyl- or 2-hydroxy-7-acyl- and 2-hydroxy-3,7-diacyl-9,10-dihydrophenanthrene are formed in varying amounts.

A structural proof for each of the described acyl derivatives has been established.

The Reaction between Diphenylketene and Certain Dienes

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The reactions between ketenes and unsaturated hydrocarbons have been studied rather extensively

(1) Abstracted from a thesis by Courtland LaVerne Agre, submitted to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Doctor of Philosophy, October, 1937.

(1a) At the time this paper was submitted, our study of the reactions of the addition product derived from diphenylketene and cyclopentadiene indicated that the structure was best represented by formula 1I. While the manuscript was in the hands of the Editor, there appeared a paper by Lewis, Ramage, Simonsen and Wainwright [J. Chem. Soc., 1837 (1937)] dealing with the same subject. From their work, the English authors were led to structure I for the adduct, and their conclusion appeared to be well founded inasmuch as they had confirmed, by independent synthesis, the structure of one of their principal degradation products. Accordingly, we have delayed publication of our paper until the completion of a further study. As one of us (C. L. A.) was no longer able to continue the work, this part of the study has been carried out with the aid of Messrs. Leekley and Prichard. Our supplementary study has led us to revise our original conclusion, and we now agree with the English authors that the structure of the adduct is undoubtedly 1. Since our method of degrading the adduct differs widely from that used by the English authors, we are now publishing our work and withdrawing from further work in the field except for the investigation of the reaction between diphenylketene and certain acetylenes, such as phenylacetylene, the study of which we have had well under way for some time.—L. I. S.

by Staudinger and his collaborators[2] who found that many unsaturated hydrocarbons would react with ketenes—notably with diphenylketene—by direct addition, to give substances that were regarded as cyclobutanone derivatives. In the case of cyclopentadiene, a very rapid addition was observed[2a] and Staudinger considered three structures (I, II, III) for the product, selecting I as best representing the structure of the compound.

However, four structures are possible for this substance (I, II, III, IV) and because of the strain inherent in such structures as I and II, it seemed more likely that the product would possess structure III or IV. Structure III is the result of a diene reaction between the two components, a reaction which has been shown to be

(2) (a) Staudinger and Suter, Ber., 53, 1092 (1920); (b) Staudinger and Rheimer, Helv. Chim. Acta, 7, 8 (1924); (c) Staudinger and Meyer, ibid., p. 19; (d) Staudinger and Meyer, Ber., 53, 72 (1920).