

several times from alcohol and from benzene. The **phenylosazone of glyoxal** was obtained in almost colorless crystals melting at 162–166°. The melting point of a mixture of this sample with an authentic one (m. p. 166–169°) was 163–167°.

The filtrate was poured into water and the solution extracted with benzene. The benzene was extracted with sodium carbonate solution. The resulting solution when acidified gave the phenylhydrazone of phenylglyoxylic acid which crystallized from benzene in bright yellow crystals melting at 159–160°. A mixture of this compound with an authentic specimen (m. p. 159–160°) melted at 159–160°.

**$\alpha$ -Phenyl- $\delta$ -benzoyl- $\delta$ -valerolactone.**—The 1,2-pyrone in methyl cellosolve was reduced catalytically in the presence of a platinum oxide catalyst. In addition to a small amount of unchanged 1,2-pyrone there were formed two hydrogenation products. These were separated by crystallization from carbon tetrachloride. The less soluble was purified by crystallization from benzene or aqueous alcohol. It melted at 137–138°. It was very soluble in alcohol, did not decolorize bromine in chloroform solution and was not attacked by chromic acid in acetic acid solution.

*Anal.* Calcd. for  $C_{18}H_{14}O_3$ : C, 77.7; H, 5.1. Found: C, 77.8; H, 5.1.

The acetate was formed by treatment with acetic anhydride and sodium acetate. It melted at 102–103°.

*Anal.* Calcd. for  $C_{20}H_{16}O_4$ : C, 75.1; H, 5.0. Found: C, 75.7; H, 5.0.

The oily residue left after the carbon tetrachloride

mother liquor had evaporated was solidified when triturated with ethyl alcohol. Recrystallization from ethyl alcohol gave the valerolactone in diamond-shaped crystals mixed with crystals of the original 1,2-pyrone. The two types of crystals were separated mechanically. The new compound when pure melted at 142–143°. It was very soluble in carbon tetrachloride and did not decolorize a solution of bromine in carbon tetrachloride.

*Anal.* Calcd. for  $C_{18}H_{16}O_3$ : C, 77.1; H, 5.8. Found: C, 77.3; H, 5.8.

In a second run in which fresh catalyst was introduced twice during the course of the hydrogenation the lactone was the only product which could be isolated.

### Summary

1,3-Dibromo-1,3-dibenzoylpropane (IV) reacts with sodium cyanide to give a mixture of the four theoretically possible 2-cyano-2-phenyl-3-bromo-5-benzoyltetrahydrofurans (V).

Treatment with alkali converts the four isomeric tetrahydrofurans into 2-cyano-2-phenyl-5-benzoyl-2,5-dihydrofuran (X).

The dihydrofuran is transformed into 3-phenyl-6-benzoyl-1,2-pyrone (XI).

Ozonolysis of the 1,2-pyrone gave glyoxal and phenylglyoxylic acid. Reduction converted the 1,2-pyrone into  $\alpha$ -phenyl- $\delta$ -benzoyl- $\delta$ -valerolactone (XII).

URBANA, ILLINOIS

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

## Studies in the Phenanthrene Series. XVIII. Synthesis of Acyl Compounds Derived from 1- and 4-Phenanthrol

BY HARRY M. DUVAL<sup>1</sup> AND ERICH MOSETTIG

In the search for substances with oestrogenic activity, the plan has been developed to synthesize more or less simple phenanthrene derivatives containing a phenolic hydroxyl group and a carbonyl group, the latter being located either in a side chain attached to, or in a five- or six-membered hydroaromatic ring condensed with, the phenanthrene nucleus.

This communication describes the preparation by means of the Fries rearrangement and the Friedel-Crafts reaction of methyl and ethyl ketones derived from 1- and 4-phenanthrol. It was found that in the "1-series" the Fries rearrangement was much superior to the Friedel-Crafts reaction. 1-Hydroxy-2-acetylphenanthrene

(1) E. R. Squibb and Sons Research Fellow.

(I) and 1-hydroxy-2-propionylphenanthrene (II) were obtained in yields of 60 and 72%, respectively, in the Fries rearrangement, and in yields of only 30 and 26% by the Friedel-Crafts reaction.

In the "4-series," 4-hydroxy- $\gamma$ -acetylphenanthrene was formed in a poor yield only (30%) in the rearrangement of 4-acetoxyphenanthrene together with a small amount (6%) of another compound that is probably 4-hydroxydiacetylphenanthrene. In the Friedel-Crafts reaction, employing acetyl and propionyl chloride, diketones could be isolated in satisfactory yield (60–70%), but no monoketones were found.

While 4-methoxyphenanthrene reacted smoothly with acetyl and propionyl chlorides in the pres-

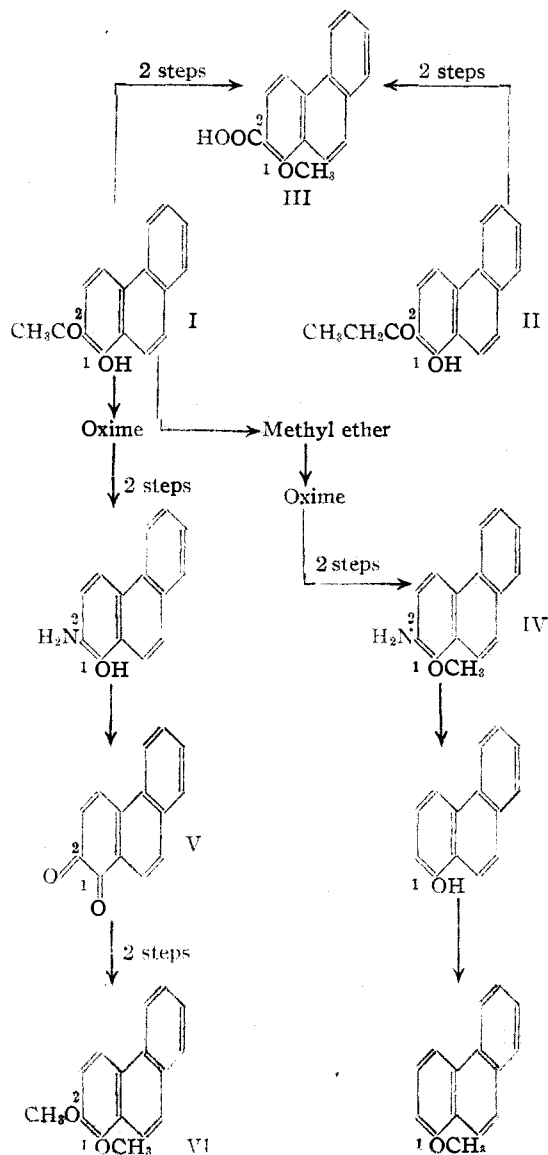
ence of aluminum chloride to give 4-methoxy-*x*-acetylphenanthrene and 4-methoxy-*x*-propionylphenanthrene in yields of 70%, the analogous reactions with 1-methoxyphenanthrene, employing the solvents nitrobenzene, *sym*-tetrachloroethane, or a mixture of both, were entirely unsuccessful, resulting only in tarry products from which no individual compounds could be isolated.

That the acyl groups in both 1-hydroxy-2-acetylphenanthrene (I) and 1-hydroxy-2-propionylphenanthrene (II) occupy the same relative position was shown by the identity of the acids resulting from the oxidation of the methylated ketones with sodium hypochlorite.

The first attempt to determine the position of the acetyl group in the ketone I, though not successful, appears to be worthy of mention. The hydroxy ketone was methylated and its oxime subjected to the Beckmann rearrangement. The resulting methoxyacetyl amino derivative was hydrolyzed and the methoxyaminophenanthrene (IV) was diazotized, with the expectation of arriving at a methoxyhydroxyphenanthrene that might be converted to a known dimethoxyphenanthrene. In the diazotization, however, elimination of the amino group, with simultaneous demethylation of the methoxyl group, took place and 1-phenanthrol was formed (identified through its methyl ether). The yield was about 10% and speculation concerning the mechanism of the formation of 1-phenanthrol seems to be, therefore, unimportant.

The structure of 1-hydroxy-2-acetylphenanthrene was established by transforming the oxime of ketone I to a hydroxyamino compound, which was oxidized with chromic acid to a quinone (V), the properties of which corresponded closely to those of 1,2-phenanthrenequinone described by Fieser.<sup>2</sup> We converted the quinone (V), via the hydroquinone, to a dimethoxy compound (VI), according to the directions of Fieser.<sup>2</sup> The latter compound (VI) was identified with an authentic sample of 1,2-dimethoxyphenanthrene, which was prepared in this Laboratory from 2-phenanthrol, according to Fieser.<sup>2</sup>

The acyl groups in 4-methoxy-*x*-acetylphenanthrene and 4-methoxy-*x*-propionylphenanthrene were shown to occupy the same relative position, by oxidation of the methoxy ketones with sodium hypochlorite to identical methoxycarboxylic acids. 4-Methoxy-*x*-acetylphenanthrene proved to be



different from the methyl ether of 4-hydroxy-*y*-acetylphenanthrene (obtained by Fries rearrangement). Thereby the difference of the location of the acetyl group in both compounds became evident.

Attempts to locate the positions *x* and *y* by various methods have been without success so far. In a series of efforts to demethylate 4-methoxy-*x*-acetylphenanthrene (30% hydrogen bromide in glacial acetic acid, concentrated hydrochloric acid in a sealed tube, aluminum chloride in benzene, phosphoric acid), the methoxy ketone either was not attacked at all, or was destroyed. With a mixture of 48% aqueous hydrobromic acid and glacial acetic acid, demethylation

(2) Fieser, THIS JOURNAL, 51, 1896 (1929).

## PHENANTHRENE DERIVATIVES

Substituent	Appearance, needles	Solvent	Yield, %	M. p., °C.	Formula	Carbon, %		Hydrogen, %	
						Calcd.	Found	Calcd.	Found
1-Hydroxy-2-acetyl <sup>a</sup>	Yellow	EtOH	60	154-155	C <sub>18</sub> H <sub>12</sub> O <sub>2</sub>	81.34	81.31	5.12	5.14
1-Hydroxy-2-propionyl <sup>b</sup>	Yellow	EtOH	72	149-150	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub>	81.58	81.82	5.64	5.99
4-Hydroxy- <i>y</i> -acetyl <sup>c</sup>	Yellow	EtOH	30	112-113	C <sub>16</sub> H <sub>12</sub> O <sub>2</sub>	81.34	81.39	5.12	5.35
4-Methoxy- <i>y</i> -acetyl <sup>d</sup>	Colorless	MeOH	Quant.	80-81.5	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub>		OCH <sub>3</sub>	12.40	11.64
4-Methoxy- <i>x</i> -acetyl <sup>e</sup>	Colorless	EtOH	73	122.5-123.5	C <sub>17</sub> H <sub>14</sub> O <sub>2</sub>	81.58	81.67	5.64	5.75
4-Methoxy- <i>x</i> -propionyl <sup>f</sup>	Colorless	EtOH	72	116	C <sub>18</sub> H <sub>16</sub> O <sub>2</sub>	81.80	81.78	6.10	6.23
4-Hydroxydiacetyl <sup>g</sup>	Yellow	EtOH	61	193	C <sub>18</sub> H <sub>14</sub> O <sub>3</sub>	77.69	77.81	5.07	5.27
Dioxime <sup>h</sup>	Yellow	EtOH	Quant.	228-229 dec.	C <sub>18</sub> H <sub>16</sub> O <sub>3</sub> N <sub>2</sub>	70.13	70.48	5.23	5.35
							N	9.09	9.00
4-Hydroxydipropionyl <sup>i</sup>	Yellow	EtOH	70	165.0-165.5	C <sub>20</sub> H <sub>18</sub> O <sub>3</sub>	78.42	78.52	5.93	5.90

<sup>a</sup> A solution of 9.00 g. of 1-acetoxyphenanthrene in 110 ml. of nitrobenzene and a solution of 11.3 g. of aluminum chloride in 45 ml. of nitrobenzene were mixed and allowed to stand for forty-eight hours. <sup>b</sup> A solution of 3.30 g. of 1-propionoxyphenanthrene (prepared from 1-phenanthrol by the action of propionyl chloride in pyridine; m. p. 94-96°) in 15 ml. of nitrobenzene and a solution of 3.87 g. of aluminum chloride in 15 ml. of nitrobenzene were mixed and allowed to stand for seventy-two hours. <sup>c</sup> A solution of 8.00 g. of 4-acetoxyphenanthrene in 60 ml. of nitrobenzene and a solution of 10.0 g. of aluminum chloride in 40 ml. of nitrobenzene were mixed and allowed to stand for forty-eight hours. A small amount of a by-product, m. p. 193-194°, was obtained. This compound was probably 4-hydroxydiacetylphenanthrene. <sup>d</sup> Prepared from 4-hydroxy-*y*-acetylphenanthrene by methylation in the usual manner. <sup>e</sup> A solution of 7.10 g. of 4-methoxyphenanthrene and 2.70 g. of acetyl chloride in 36 ml. of nitrobenzene and a solution of 10.0 g. of aluminum chloride in 35 ml. of nitrobenzene were mixed and allowed to stand for forty-eight hours. <sup>f</sup> A solution of 4.00 g. of 4-methoxyphenanthrene and 1.84 ml. of propionyl chloride in 20 ml. of nitrobenzene and a solution of 5.64 g. of aluminum chloride in 20 ml. of nitrobenzene were mixed and allowed to stand for forty-eight hours. <sup>g</sup> A solution of 9.00 g. of 4-acetoxyphenanthrene and 3.96 ml. of acetic anhydride in 45 ml. of nitrobenzene and a solution of 11.3 g. of aluminum chloride in 45 ml. of nitrobenzene were mixed and allowed to stand for forty-eight hours. <sup>h</sup> Prepared from 4-hydroxydiacetylphenanthrene in the usual manner. <sup>i</sup> A solution of 6.40 g. of 4-phenanthrol and 6.31 ml. of propionyl chloride in 32 ml. of nitrobenzene and a solution of 9.70 g. of aluminum chloride in 32 ml. of nitrobenzene were mixed and allowed to stand for seventy-two hours.

was effected, but only with simultaneous elimination of the acetyl group.<sup>3</sup>

Furthermore, 4-methoxy-*y*-acetylphenanthrene was converted, through the oxime, and the rearrangement of the latter, to 4-methoxy-*x*-amino-phenanthrene. It was planned to demethylate this compound and oxidize the expected hydroxy amine to a quinone. Unfortunately, we were un-

(3) An analogous elimination has been observed recently by Robinson and Walker, *J. Chem. Soc.*, 185 (1938). 1-Acetyl-2-hydroxynaphthalene, by boiling with hydriodic acid, readily gave 2-hydroxynaphthalene. See also Hill, Short and Stromberg, *ibid.*, 1619 (1937).

able to effect demethylation under varied experimental conditions.

It is not unlikely that one of the two positions, *x* and *y*, is position 1, and the other is position 3. Further, we believe it probable that in the diacetyl compound, at least one of the acetyl groups is located in position *x* or *y*.

Attempts to elucidate the structures of the compounds in the 4-series are being continued.

## Experimental

1- and 4-acetoxyphenanthrene were prepared by boiling under reflux for five hours a solution of five parts of the respective phenanthrol and one part of anhydrous sodium acetate in fifty parts of acetic anhydride. The reaction mixture, after cooling to room temperature, was poured into water, whereupon the acetoxyphenanthrene separated in a practically pure state; m. p. 131-134, and 58-60°, respectively; yields, nearly quantitative.

1- and 4-methoxyphenanthrene were prepared, according to the method of Stevens and Tucker,<sup>4</sup> by adding dimethyl sulfate dropwise, with vigorous stirring, to a suspension of the acetoxyphenanthrene in a mixture of 66% potassium hydroxide solution and acetone (by weight, 1 part of acetoxyphenanthrene and 2.80 parts of potassium hydroxide; by volume, 1.45 parts of water, 10 parts of acetone and 1.60 parts of dimethyl sulfate). The reaction mixture was then poured into a large excess of water. The methyl ethers were obtained in a practically pure state (m. p. 101-103, and 65-67°, respectively), and were crystallized once from ethyl and methyl alcohol, respectively. The yields were nearly quantitative.

All other methylations cited in this communication were carried out by the procedure described above.

**Friedel-Crafts Reaction.**—Hydroxy-, acetoxy- or methoxyphenanthrene was dissolved in nitrobenzene and to the solution was added one or two moles, plus 10% excess, of acid chloride or acid anhydride. A solution of two moles, plus 10% excess, of aluminum chloride in nitrobenzene was poured slowly into the first solution, both solutions having been cooled previously in an ice-bath. The reaction mixture was kept at 0-5° for forty-eight or seventy-two hours and then decomposed by pouring onto ice and concentrated hydrochloric acid. The nitrobenzene was removed by steam distillation.

The reaction product from methoxyphenanthrene was

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

purified by crystallization from alcohol, with use of Norite.

The reaction product from hydroxy- and acetoxyphenanthrenes was dissolved in an excess of 5% potassium hydroxide solution and alcohol, heated to boiling, to ensure complete saponification of any ester present. The hot solution was filtered and, after cooling to room temperature, acidified with concentrated hydrochloric acid. The hydroxyacylphenanthrene thus precipitated was collected and purified by crystallization from alcohol, with the use of Norite.

**Fries Rearrangement.**—The experimental procedure for the Fries rearrangement differed from that described for the Friedel-Crafts reaction only in that no acid chloride or acid anhydride was used.

#### Proof of Structure

**1-Methoxyphenanthrene-2-carboxylic Acid (III).**—A suspension of 0.20 g. of the methyl ether of ketone I (m. p. 80–81°) in 38 ml. of a 1% aqueous hypochlorite solution was boiled under reflux until a practically clear solution resulted. (The hypochlorite solution was prepared from calcium hypochlorite "HTH" and sodium carbonate.) The hot reaction mixture was filtered and cooled, and two grams of sodium thiosulfate was added. The acid (III), along with some sulfur, was liberated by acidification with concentrated hydrochloric acid. The sulfur was removed by digesting the precipitate with saturated sodium bicarbonate solution and filtering the solution while hot. The acid was regenerated by acidifying the filtrate at room temperature. Crystallized from alcohol, the acid was obtained as colorless needles; m. p. 224–225° (dec.).

*Anal.* Calcd. for  $C_{16}H_{12}O_3$ : C, 76.18; H, 4.79. Found: C, 76.17; H, 5.12.

The same acid was obtained by hypochlorite oxidation of the methyl ether of ketone II (m. p. 74–76°). The identity of these two acids was established by their melting points (224.5 and 223–224°, respectively) and a mixture melting point determination (224–225°) and by the melting points (109–110 and 109°) and mixture melting point (109–110°) of their respective methyl esters.

**1-Methoxy-2-acetylphenanthrene.**—The methyl ether of ketone I was prepared in quantitative yield by the methylation procedure described above. Crystallized from methyl alcohol, it was obtained as colorless plates; m. p. 81–82°.

*Anal.* Calcd. for  $C_{17}H_{14}O_2$ :  $OCH_3$ , 12.40. Found:  $OCH_3$ , 12.12.

**Oxime.**—A solution of one molecular equivalent of the above ketone, two moles of hydroxylamine hydrochloride and two and one-half moles of anhydrous sodium acetate in alcohol was boiled under reflux for four hours. The solution was then concentrated, cooled to room temperature and diluted with water until the oxime had separated completely. The yield was quantitative. Crystallized from methyl alcohol, the oxime was obtained as colorless needles; m. p. 166–167° (dec.).

*Anal.* Calcd. for  $C_{17}H_{16}O_2$ : N, 5.28. Found: N, 5.47.

**1-Methoxy-2-acetylaminophenanthrene.**—A solution of 1.00 g. of the above oxime in a mixture of 5 ml. of glacial acetic acid and 5 ml. of acetic anhydride was saturated with dry hydrogen chloride. The reaction mixture, now a

solid paste, was allowed to stand for twenty hours, and was then poured onto ice and water. The acetyl amino compound was collected, washed with water and dried; m. p. 220–222° (dec.). The yield was quantitative. After crystallization from methyl alcohol, 1-methoxy-2-acetylaminophenanthrene was obtained as colorless plates; m. p. 222–223° (dec.).

*Anal.* Calcd. for  $C_{17}H_{16}O_2$ : N, 5.28. Found: N, 5.12.

**1-Methoxy-2-aminophenanthrene (IV).**—A solution of 0.90 g. of the above N-acetylamine in a mixture of 10 ml. of 6 N hydrochloric acid and 10 ml. of glacial acetic acid was boiled under reflux for one hour. The amine hydrochloride, which separated on cooling the reaction mixture, was filtered off and converted to the free base by treatment with ammonium hydroxide. The amine (IV), obtained in a yield of 87%, was crystallized from alcohol: colorless needles, m. p. 139.5–141°.

*Anal.* Calcd. for  $C_{16}H_{13}ON$ : C, 80.70; H, 5.87; N, 6.27;  $OCH_3$ , 13.90. Found: C, 80.63; H, 5.93; N, 6.41;  $OCH_3$ , 13.34.

The amine was diazotized according to the method of De Milt and van Zandt.<sup>5</sup> A solution of 0.50 g. of the amine in 2.3 ml. of pyridine was added slowly (one hour) to a solution of nitrosyl sulfuric acid cooled to 0° with ice and salt. (The nitrosyl sulfuric acid solution was prepared by first adding 0.34 g. of sodium nitrite to a cold mixture of 3.4 ml. of concentrated sulfuric acid and 1.7 ml. of water, and then carefully warming the mixture to 40° until a clear solution resulted.) The mixture was stirred for an hour at 0° and then was diluted with ice and water to a volume of about 100 ml. An aqueous solution of 0.22 g. of urea was added and stirring was continued for another hour at 0°. The solution of the diazonium sulfate was filtered and added, in small portions, to 300 ml. of boiling water. Boiling was continued for about fifteen minutes. After standing overnight, the precipitate which had separated was filtered off and dissolved in 5% potassium hydroxide solution. The filtered alkaline solution was acidified with concentrated hydrochloric acid and the phenolic product (0.06 g.) thus obtained was methylated in the usual manner. The methylated product was purified by sublimation and crystallization and melted at 102–103°. It was shown to be 1-methoxyphenanthrene; a mixture melting point determination with an authentic sample (m. p. 103–104°) showed no depression (m. p. 103°).

**Oxime of I.**—The oxime of ketone I was prepared in the usual manner, yield quantitative. When first isolated, the oxime was nearly colorless, but it turned yellow on short standing. It crystallized from alcohol in yellow needles, m. p. 224–225° (dec.).

*Anal.* Calcd. for  $C_{16}H_{13}O_2N$ : C, 76.48; H, 5.21; N, 5.58. Found: C, 76.57; H, 5.42; N, 5.40.

**1,2-Dimethoxyphenanthrene (VI).**—A solution of 3.84 g. of the above oxime and 4 g. of phosphorus pentachloride in 500 ml. of dry benzene was boiled under reflux for thirty minutes, according to the method of Bachmann and Boatner.<sup>6</sup> The solution, after cooling to room temperature, was extracted with water, sodium bicarbonate solu-

(5) De Milt and van Zandt, *THIS JOURNAL*, **53**, 2044 (1936); see also Bachmann and Boatner, *ibid.*, **58**, 2194 (1936).

(6) Bachmann and Boatner, *ibid.*, **58**, 2097 (1936).

tion and water again to remove phosphorus compounds. The dried benzene solution yielded 3.12 g. of crude 1-hydroxy-2-acetylaminophenanthrene.

The crude hydroxyacetylaminophenanthrene was hydrolyzed to the corresponding amine hydrochloride by boiling under reflux for one hour with 28 ml. of 6 *N* hydrochloric acid and 28 ml. of glacial acetic acid. The reaction mixture, after cooling in an ice-bath, was diluted with several volumes of water, and the amine hydrochloride which had separated was collected; yield 2.31 g.

The amine hydrochloride was converted, through the quinone (V) and the hydroquinone, to 1,2-dimethoxyphenanthrene (VI), according to the directions of Fieser,<sup>2</sup> as given for the analogous conversion of 1-amino-2-hydroxyphenanthrene hydrochloride to 1,2-dimethoxyphenanthrene. The dimethoxyphenanthrene thus obtained, after purification by sublimation and crystallization, melted at 103–104° (corr.). A mixture melting point determination with an authentic sample (m. p. 103–104°) showed no depression (m. p. 103–104°).

*Anal.* Calcd. for  $C_{16}H_{14}O_2$ :  $OCH_3$ , 26.05. Found:  $OCH_3$ , 25.91.

Samples of 1,2-phenanthrenequinone (V) from the above hydroxyamine hydrochloride and from 1-amino-2-hydroxyphenanthrene hydrochloride were purified by sublimation and crystallization. Both samples were brilliant red in color and gave in concentrated sulfuric acid the characteristic color change from blue to green. We found the melting point of both samples of the quinone to be indefinite and unsatisfactory for the purpose of identification (the quinone did not soften, but decomposed over a variable range of about ten to twenty degrees, starting at 190–195°).

**4-Methoxyphenanthrene-*x*-carboxylic Acid.**—4-Methoxy-*x*-acetylphenanthrene was oxidized to the corresponding carboxylic acid by the hypochlorite method described above. The acid, crystallized from toluene as colorless needles, melted at 238–239°.

*Anal.* Calcd. for  $C_{16}H_{12}O_3$ : C, 76.18; H, 4.79. Found: C, 76.92; H, 5.32.

The same acid was obtained by hypochlorite oxidation of 4-methoxy-*x*-propionylphenanthrene. The identity of these two acids was established by their melting points (238–239°) and a mixture melting point (238–239°).

**Methyl Ester.**—Both acids described above, from 4-methoxy-*x*-acetylphenanthrene and from 4-methoxy-*x*-propionylphenanthrene, were methylated in the usual manner. Both esters, crystallized from methyl alcohol and obtained as colorless needles, melted at 93–94°. A mixture melting point determination showed no depression (m. p. 93–94°).

*Anal.* Calcd. for  $C_{17}H_{14}O_3$ : C, 76.68; H, 5.30. Found: C, 76.63; H, 5.36.

**Oxime of 4-Methoxy-*x*-acetylphenanthrene.**—This oxime was prepared in the usual manner from 4-methoxy-*x*-acetylphenanthrene, yield quantitative. It crystallized from ethyl alcohol as colorless needles of m. p. 190–191° (dec.).

*Anal.* Calcd. for  $C_{17}H_{15}O_2N$ : N, 5.28. Found: N, 5.11.

**4-Methoxy-*x*-acetylaminophenanthrene.**—The above oxime rearranged to 4-methoxy-*x*-acetylaminophenanthrene in quantitative yield by the glacial acetic acid-acetic anhydride-hydrogen chloride method already described. Crystallized from methyl alcohol, the *N*-acetyl amino compound appeared as colorless needles of m. p. 201°.

*Anal.* Calcd. for  $C_{17}H_{15}O_2N$ : N, 5.28. Found: N, 5.44.

## Summary

1. A series of acyl compounds derived from 1- and 4-phenanthrol has been synthesized by means of the Fries rearrangement and the Friedel-Crafts reaction.
2. 1-Hydroxy-2-acetylphenanthrene and 1-hydroxy-2-propionylphenanthrene have been described and their structures have been established.
3. 4-Hydroxy-*y*-acetylphenanthrene, 4-hydroxydiacetylphenanthrene, 4-hydroxydipropionylphenanthrene, 4-methoxy-*x*-acetylphenanthrene and 4-methoxy-*x*-propionylphenanthrene have been described.