When an excess of alkali was used for neutralization of the lactone a substance was formed which was not the sodium salt of the hydroxy acid. This substance was insoluble in alcohol or water.

α-Ethyl γ-Butyrolactone.—This compound was prepared from ethyl, ethylvinyloxyethyl malonate[5] in the same manner as γ-butyrolactone except that the saponification was conducted in alcoholic solution. From 12 g. of the malonic ester 2.8 g. of product was obtained boiling at 214–218°. The yield was 59% of the theoretical.

α-Propyl-γ-butyrolactone was prepared as above from ethyl propylvinyloxyethyl malonate.[5] The product boiled at 230–235°; d_4^{25} 1.008. The yield was 63% of the theoretical.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.57; H, 9.45. Found: C, 65.23; H, 9.34.

Neutralization equivalent. Calcd.: 128.1. Found: 127.8.

Summary

A method is described for the preparation of γ-butyrolactone and its α-alkyl derivatives.

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SYNTHESES IN THE PHENANTHRENE SERIES.
I. ACETYLPHENANTHRENES[1]

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The preparation of 9-acetylphenanthrene was described by Willgerodt and Albert[2] in 1911. These authors obtained the substance by the Friedel–Crafts reaction, and describe it as fluorescent leaflets of melting point 123°. Analysis and the formation of an oxime and a phenylhydrazone showed the compound to be a phenanthryl methyl ketone. Oxidation with chromic acid led exclusively to 9,10-phenanthrenequinone, showing that the acetyl group occupied the 9-position on the phenanthrene nucleus. The authors do not mention the yields obtained, but from their description it is to be gathered that the ketone is very difficult to obtain in a pure state because of accompanying oils and tarry material.

In attempting to prepare 9-acetylphenanthrene according to Willgerodt's directions, we have obtained results differing considerably from those mentioned above. Acetylation of phenanthrene with acetyl chloride and aluminum chloride in carbon disulfide solution, under Willgerodt's conditions, gave a small amount of crystalline material, together with resinous products and a considerable quantity of a thin oil. From the oil a small quantity of a ketone could be isolated as the semicarbazone; the oil dis-

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[5] Cretcher, Koch and Pittenger, THIS JOURNAL, **47**, 3083 (1925).

[1] These researches have been supported by the Committee on Drug Addiction of the National Research Council.

[2] Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).

tilled almost undecomposed in vacuum, but boiled over such a wide range that further investigation has been delayed.

The crystalline portion, which was obtained in a yield averaging 5 to 10% (in one experiment which could not be duplicated, 50–60%), melted from 60 to 80° and contained some phenanthrene. Since this could not be removed by crystallization, the mixture was treated with semicarbazide. The semicarbazone proved, however, to be heterogeneous, and from it by laborious fractional crystallization two different semicarbazones could be obtained. When these were decomposed with hydrochloric or oxalic acid, two ketones of m. p. 72 and 143° were isolated. It therefore seemed desirable to improve the method of preparation of the ketones.

Lowering the temperature to 0 or to $-15°$ gave no better results; substitution of aluminum bromide and acetyl bromide decreases the yield; stannic chloride as catalyst, or acetic anhydride in place of acetyl chloride, according to Adams,[3] were likewise without favorable result.

When, however, nitrobenzene was used as a solvent, the mixture of ketones was obtained in about 80% yield. The separation of these was accomplished through the difference in solubilities in methyl and ethyl alcohol. The sparingly soluble ketone (yield 15%) melts at 143°, the more soluble isomer (yield 63.5%) at 72°.

To determine the position occupied by the acetyl group, the isomers were oxidized with 2% sodium hypochlorite solution according to Graebe[4] ($RCOCH_3 + 3\ NaOCl \longrightarrow RCOONa + 2\ NaOH + CHCl_3$), to the corresponding carboxylic acids.

The 72° ketone gave an acid of m. p. 270°, whose methyl and ethyl esters melted at 94.5–95° and 56–57°, respectively. The acid gives a very characteristic potassium salt.

The 143° ketone yielded an acid melting at 258.5 to 260°, whose methyl and ethyl esters melted at 96–96.5° and 73–73.5°, respectively. The sodium salt is very sparingly soluble in water, the potassium salt nearly insoluble.

The properties of the acids, their esters and salts pointed to their identity with the phenanthrene-2- and 3-carboxylic acids of Werner[5] and Fieser.[6]

Phenanthrene-9-carboxylic acid, prepared according to Pschorr,[7] was found by direct comparison of properties and mixed melting points to be different from the acids prepared from the two ketones. Therefore, in neither of these ketones does the acetyl group occupy the 9-position.

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[3] Adams and Noller, THIS JOURNAL, **46**, 1889 (1924).

[4] Graebe, *Ber.*, **35**, 2753 (1902).

[5] Werner, *Ann.*, **321**, 248 (1902), gives the m. p. 254° for phenanthrene-2-carboxylic acid, and emphasizes the slight solubility of the potassium salt. For the 3-carboxylic acid, the m. p. 269° is given.

[6] Fieser, THIS JOURNAL, **51**, 3101 (1929), gives the m. p. of phenanthrene-3-carboxylic acid methyl ester as 97°.

[7] Pschorr, *Ber.*, **29**, 497 (1896).

To prove that the acids derived from our two acetylphenanthrenes were actually the phenanthrene-2- and 3-carboxylic acids, these were synthesized by the method of Werner.[8]

Phenanthrene was sulfonated by Fieser's[9] modification of Werner's procedure. Under certain conditions, practically the only monosulfonic acids obtained are the 2- and 3-forms. The position of the sulfonyl groups in these acids, and consequently of the carboxyl groups in the carboxylic acids derived from them seems to be sufficiently proved by Werner's researches. That we were actually working with the pure sulfonic acids was proved by the preparation of the *p*-toluides (Fieser) and the methyl esters (Werner).

The phenanthrene-carboxylic acid prepared from the 2-sulfonic acid agreed in all characteristic properties and derivatives with that obtained by oxidation of the ketone melting at 143°; the carboxylic acid from the 3-sulfonic acid was similarly shown to be identical with the one obtained from our 72° ketone. On the basis of Werner's proof of the structure of these two sulfonic acids, therefore, we assign to the sparingly soluble ketone of melting point 143° the structure of 2-acetylphenanthrene; to the more soluble ketone of melting point 72°, the structure of 3-acetylphenanthrene.

Oxidation of the acetylphenanthrenes with chromic acid converts them smoothly into the 2-, and 3-acetylphenanthrene-9,10-quinones, respectively.

We have not yet been able to isolate any other acetylphenanthrene isomer from the reaction. Very small amounts (0.1%) of a third substance, crystallizing in needles of melting point 279–280° were found, whose nature has not yet been determined.

Attempts to synthesize, from 9-substituted phenanthrene derivatives, the 9-acetylphenanthrene which was expected from Willgerodt's procedure have so far been fruitless. These experiments as well as those designed to introduce two acetyl groups and one or more benzoyl groups into the phenanthrene nucleus are being continued.

The marked favoring of the 2- and 3-positions observed in the above Friedel–Crafts acetylation over the 9-position, preference for which would be expected[10] from the presence of the 9,10-double bond, which recalls in many respects an olefinic double bond, is remarkable, and is not easy to bring into accord with the results of bromination,[11] nitration[12] and sulfonation.[13]

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[8] Ref. 5, pp. 326, 330.

[9] Fieser, THIS JOURNAL, **51**, 2460 (1929).

[10] *Cf.* Wieland and Bettag, "Zur Kenntnis der Friedel–Crafts'schen Reaktion," *Ber.*, **55**, 2246 (1922).

[11] Hayduck, *Ann.*, **167**, 180 (1873); *et al.*

[12] Schmidt, *Ber.*, **33**, 3251 (1900); Wieland and Rahn, *ibid.*, **54**, 1770 (1921).

[13] *Cf.* Fieser, "The Sulfonation of Phenanthrene. II. Disulfonation," THIS JOURNAL, **51**, 2471 (1929).

It is possible that an investigation of the oil which appears in such large quantities in the customary procedure in carbon disulfide solution will give further information. The extent to which the nitrobenzene used as solvent influences the reaction in a qualitative or quantitative way is difficult to estimate.

Experimental Part

The phenanthrene used in the experiments described below was a purified product of m. p. 98–99°; the nitrobenzene was dried over calcium chloride.

2- and 3-Acetylphenanthrenes, $C_{14}H_9COCH_3$.—One hundred and thirty-two grams of finely powdered aluminum chloride was added in small portions to 600 g. of nitrobenzene, and the resulting clear solution then mixed with a solution of 80 g. of phenanthrene in 240 g. of nitrobenzene. The solution was cooled in ice water and 48 g. of freshly-distilled acetyl chloride was added all at once. After half an hour's standing in ice water, the dark clear solution stood at room temperature (25°) for six to seven hours. It was poured into a large amount of ice and treated with 80 cc. of concentrated hydrochloric acid. In all, 400 g. of phenanthrene, in five lots, was so treated, and the united products distilled with steam to remove nitrobenzene as completely as possible. The distillation residue was a dark brown viscous mass which on digestion with ether largely went into solution. The ether-insoluble portion, a dark crystalline mass, was purified in two ways.

(1) It was spread on a clay plate to remove oils and then refluxed with animal charcoal in methyl alcohol. From the filtrate the 2-acetylphenanthrene separated in nearly pure, faintly colored, thick needles, of m. p. 138–142°. The methyl alcohol-insoluble carbonaceous mass weighed 5 g. After two recrystallizations from methyl or ethyl alcohol or benzene, the ketone was obtained pure white, m. p. 143° (corr.).

(2) To avoid the purification with methyl alcohol, in which the 2-acetylphenanthrene is very sparingly soluble (benzene cannot be used, because it dissolves the impurities as well), the ether residue above was twice distilled at a pressure of 2–3 mm. in a sabre flask. The colorless distillate crystallized immediately and was purified from benzene. The two methods gave about the same yields.

3-Acetylphenanthrene, $C_{14}H_9COCH_3$.—The ethereal solution from extraction of the steam distillation residue above was dried over sodium sulfate and the ether distilled off. The residue solidified soon to clumps of crystals. From methyl alcohol this separated only as an oil; it was therefore extracted in a Soxhlet apparatus with petroleum ether (b. p. 40–60°), leaving a very small portion undissolved. After removal of the petroleum ether, the product was distilled at 2–3 mm., giving an oil which soon crystallized. This could be recrystallized from methyl alcohol, in which it is very soluble, yielding 3-acetylphenanthrene as clumps of needles, m. p. 72°.

In this crystallization a small amount (0.5 g.) of a nearly insoluble substance was obtained as long thin white needles of m. p. 279–280° (uncorr.), which has not yet been identified. Traces of the 2-acetyl compound were also found at this point.

From 400 g. of phenanthrene, 315 g. of pure 3-acetylphenanthrene (63.5%), 75 g. of pure 2-acetylphenanthrene (15%), and 0.5 g. of the 280° product were obtained.

2-Acetylphenanthrene is soluble with difficulty in methyl or ethyl alcohol, petroleum ether or ligroin, more soluble in benzene or glacial acetic acid.

Anal. Subs., 0.0777: CO_2, 0.2471; H_2O, 0.0397. Calcd. for $C_{16}H_{12}O$: C, 87.23; H, 5.50. Found: C, 86.73; H, 5.72.

2-Acetylphenanthrene Semicarbazone.—One-half gram of the ketone was dissolved in hot alcohol and treated with 10% more than the calculated amount of semicarbazide hydrochloride and sodium acetate in concentrated aqueous solution. The mixture was warmed for ten minutes and after a short time the semicarbazone separated crystalline. It crystallizes from alcohol, in which it is only slightly soluble, in leaflets. After drying in vacuum at 100°, it melted at about 260° with gas evolution, then solidified and melted again at 297–299° (uncorr.) with decomposition. The same melting phenomenon was shown in a vacuum melting point tube.

Anal. Subs., 4.994 mg.: 0.678 cc. of N (27°, 747 mm.). Calcd. for $C_{17}H_{15}ON_3$: N, 15.16. Found: N, 15.18.

2-Acetylphenanthrene Phenylhydrazone.—A hot glacial acetic acid solution of 0.5 g. of ketone was treated with a hot solution of 0.27 g. (10% excess) of phenylhydrazine in glacial acetic acid. The phenylhydrazone separated after a short time in faintly yellow, shining leaflets, which were washed with a little acetic acid; m. p. in evacuated tube, 187–188° (corr.), turning brown.

Anal. Subs., 5.009 mg.: 0.406 cc. of N (27°, 750 mm.). Calcd. for $C_{22}H_{18}N_2$: N, 9.03. Found: N, 9.10.

Oxidation with Chromic Acid

2-Acetylphenanthrene-9,10-quinone, $C_{14}H_7O_2COCH_3$.—One gram of ketone was warmed to solution in 20 cc. of glacial acetic acid and treated with 1.0 g. of chromic anhydride in 2 cc. of water and 5 cc. of glacial acetic acid, not permitting the temperature to rise above 80°. After ten minutes at 70–80°, the solution was cooled and the quinone separated as a fine crystalline precipitate. Recrystallized from glacial acetic acid, it formed fine orange-yellow needles, melting in vacuum at 223–224° (corr.) (sintering at 218°).

Anal. Subs., 0.1015: CO_2, 0.2862; H_2O, 0.0389. Calcd. for $C_{16}H_{10}O_3$: C, 76.78; H, 4.03. Found: C, 76.90; H, 4.29.

Oxidation with Sodium Hypochlorite

Phenanthrene-2-carboxylic Acid, $C_{14}H_9COOH$.—A suspension of 3.0 g. of ketone in somewhat more than the calculated amount of 2% aqueous sodium hypochlorite solution was boiled gently for three hours. After an hour, the sparingly soluble sodium salt of phenanthrene-2-carboxylic acid began to separate. The odor of chloroform was perceptible during the reaction. At the end of the oxidation sufficient water was added to dissolve the salt and the unchanged ketone shaken out into ether. The acid was precipitated from the aqueous solution by hydrochloric acid; the yield of the crude dry product was 70% of the theoretical. It was recrystallized from glacial acetic acid, m. p. 258.5–260° (uncorr.). It was analyzed in the form of its esters.

Phenanthrene-2-carboxylic Acid Ethyl Ester.—One gram of the acid in 20 cc. of absolute alcohol with 1.5 g. of concentrated sulfuric acid was refluxed for three hours. After removal of most of the alcohol in vacuum, the residue was poured into a large amount of water, whereupon the ester separated crystalline. It was extracted into ether and freed from unchanged acid by shaking with dilute sodium hydroxide. The residue from the ether was recrystallized from petroleum ether as white needles of m. p. 73–73.5°. The yield was nearly quantitative.

Anal. Subs., 0.1289: CO_2, 0.3844; H_2O, 0.0695. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.33; H, 6.03.

Phenanthrene-2-carboxylic Acid Methyl Ester.—This was prepared by esterification with methyl alcohol, in the manner described above. It was recrystallized from methyl alcohol, and consisted of white needles, m. p. 96–96.5° (corr.), yield quantitative.

Anal. Subs., 0.1130: CO_2, 0.3363; H_2O, 0.0533. Calcd. for $C_{16}H_{12}O_2$: C, 81.32; H, 5.12. Found: C, 81.17; H, 5.28.

Phenanthrene-2-carboxylic Acid Amide, $C_{14}H_9CONH_2$.—The amide was prepared from the acid chloride by the action of ammonia. Five grams of the acid was boiled for one and one-half hours with five times the calculated amount of thionyl chloride. By evaporation of the excess thionyl chloride in vacuum, a slightly colored crystalline acid chloride resulted directly, which was used without further purification. One gram of the crude acid chloride was added to a solution of 0.5 g. of sodium hydroxide in 12 cc. of 20% ammonia. This was warmed for three and one-half hours on the steam-bath with frequent shaking and addition of two 5-cc. portions of 20% ammonia. The precipitate of the amide was filtered out and washed with water. Only traces of the carboxylic acid could be detected with hydrochloric acid in the filtrate. The amide crystallizes from methyl alcohol or benzene, in which it is sparingly soluble, in silky white needles of m. p. 242–243° (corr.).

Anal. Subs., 4.512 mg.: 0.259 cc. of N (25°, 755 mm.). Calcd. for $C_{15}H_{11}ON$: N, 6.33. Found: N, 6.53.

For comparison with the product obtained from oxidation of the 2-ketone, phenanthrene-2-carboxylic acid was prepared from barium phenanthrene-2-sulfonate.[5,6] This yielded on dry distillation with potassium ferrocyanide the phenanthryl-2-cyanide, agreeing in melting point with Werner's[5] cyanide (104.5–105° corr.). The acid obtained by hydrolysis of the cyanide was identical with that from the 2-ketone, as shown by mixed melting point and mixed melting point of the methyl esters. The extreme insolubility of the potassium salt is noteworthy.

3-Acetylphenanthrene, $C_{14}H_9COCH_3$.—Isolation as described above; m. p. 72°; white needles, quite soluble in methyl or ethyl alcohol, glacial acetic acid or benzene; soluble with difficulty in petroleum ether.

Anal. Subs., 0.0972: CO_2, 0.3100; H_2O, 0.0482. Calcd. for $C_{16}H_{12}O$: C, 87.23; H, 5.50. Found: C, 86.98; H, 5.55.

3-Acetylphenanthrene Semicarbazone.—White needles of m. p. 228–230° (corr.), sparingly soluble in alcohol.

Anal. Subs., 5.045 mg.: 0.689 cc. of N (29°, 749 mm.). Calcd. for $C_{17}H_{15}ON_3$: N, 15.16. Found: N, 15.21.

3-Acetylphenanthrene Phenylhydrazone.—Faintly yellow needles of m. p. 192.5–194° (corr.) in vacuum.

Anal. Subs., 4.845 mg.: 0.389 cc. of N (26°, 753 mm.). Calcd. for $C_{22}H_{18}N_2$: N, 9.03. Found: N, 9.08.

3-Acetylphenanthrene-oxime.—A solution of 1.0 g. of 3-ketone in 15 cc. of alcohol was treated with an aqueous solution of 0.7 g. of hydroxylamine hydrochloride (2 moles), neutralized with sodium carbonate and refluxed for one hour. After filtering from the sodium chloride, the reaction mixture deposited needles; recrystallized twice from methyl alcohol, these melted at 143.5–144° (corr.).

Anal. Subs., 4.588 mg.: 0.241 cc. of N (24°, 754 mm.). Calcd. for $C_{16}H_{13}ON$: N, 5.96. Found: N, 5.99.

From the mother liquors from the preparation of the oxime a more soluble substance of m. p. 181–182° (uncorr.) could be obtained in very small quantities. It is possible that this represents a stereoisomeric oxime; the small quantity available was not obtained pure enough for analysis.

3-Acetylphenanthrene Picrate.—The picrate was obtained by mixing hot alcoholic solutions of the calculated amounts of the components. It consisted of bright yellow needles of m. p. 125–125.5° (corr.).

Anal. Subs., 5.079 mg.: 0.411 cc. of N (24°, 755 mm.). Calcd. for $C_{22}H_{15}O_8N_3$: N, 9.36. Found: N, 9.24.

Oxidation with Chromic Acid

3-Acetylphenanthrene-9,10-quinone.—The oxidation was carried out like that of the 2-ketone; because of its greater solubility, the quinone must in this case be precipitated out with water. It crystallizes in brick-red needle rosets from glacial acetic acid, m. p. 217–218.5° (corr.) in vacuum (sintering at 214°).

Anal. Subs., 0.1307: CO_2, 0.3681; H_2O, 0.0500. Calcd. for $C_{16}H_{10}O_3$: C, 76.78; H, 4.03. Found: C, 76.81; H, 4.28.

Oxidation with Sodium Hypochlorite

Phenanthrene 3-Carboxylic Acid.—The oxidation, carried out as in the case of the 2-acetyl compound, gave a 75% yield of the 3-carboxylic acid as white needles, very sparingly soluble in glacial acetic acid, and melting at 270° (uncorr.).

Phenanthrene 3-Carboxylic Acid Ethyl Ester.—White needles from petroleum ether, of m. p. 56–57° (corr.).

Anal. Subs., 0.1278: CO_2, 0.3829; H_2O, 0.0671. Calcd. for $C_{17}H_{14}O_2$: C, 81.56; H, 5.64. Found: C, 81.71; H, 5.88.

Phenanthrene 3-Carboxylic Acid Methyl Ester.—White needles from methyl alcohol, m. p. 94.5–95° (corr.). (Recently prepared by Fieser[6] from the silver salt and methyl iodide.)

Phenanthrene-3-carboxylic acid amide (prepared from the crude acid chloride) melts at 233–234° (corr.); Werner gives the melting point as 228° (uncorr.).

For comparison, phenanthrene-3-carboxylic acid was prepared according to Werner, from potassium phenanthrene-3-sulfonate, and was found to agree in properties. Potassium phenanthrene-3-carboxylate crystallizes in unusual form, hair-like needles, bowed into semicircular form. No depression was observed in a mixed melting point of the free acids, esters or amides.

Phenanthrene-9-carboxylic Acid Methyl Ester.—White needles from methyl alcohol, m. p. 116° (corr.).

Anal. Subs., 0.1155: CO_2, 0.3443; H_2O, 0.0562. Calcd. for $C_{16}H_{12}O_2$: C, 81.32; H, 5.12. Found: C, 81.30; H, 5.44.

Phenanthrene-9-carboxylic Acid Amide.—The amide was prepared from the crude acid chloride with ammonia. It crystallizes from benzene in silky needles of m. p. 232–233° (corr.).

Anal. Subs., 5.145 mg.: 0.289 cc. of N (24°, 755 mm.). Calcd. for $C_{15}H_{11}ON$: N, 6.33. Found: N, 6.41.

Summary

The preparation of 2-acetylphenanthrene and 3-acetylphenanthrene in satisfactory yields has been described.

Through the smooth oxidation of the acetyl derivatives to the carboxylic acids, a good preparative way to phenanthrene-2-carboxylic acid and phenanthrene-3-carboxylic acid is opened.

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