retarded. By operation of the above procedure at 30° for 1.5 hr., there was obtained after recrystallization from isobutanol, 3850 g. (87%) of I ($n = 6$, R = i-C_4H_9), m.p. 165–166°.

d. *Mixed anhydride method.* p-Carboisobutoxybenzoic acid, 22.2 g. (0.1 mole), was dissolved in 100 ml. of dry chloroform and the solution cooled to 0°. Triethylamine, 10.1 g. (0.1 mole), was then added, followed by 10.8 g. (0.1 mole) of ethyl chlorocarbonate. The mixture was maintained at 0–5° for 2 hr., at which time a solution of 5.3 g. (0.05 mole) of hexamethylenediamine in 30 ml. of dry chloroform was added. The temperature of the mixture rose rapidly to 30° and carbon dioxide was evolved. The reaction mixture was allowed to stand at 5° for 18 hr. at which time the chloroform solution was washed with water and dilute sodium carbonate. The chloroform solution was dried over potassium carbonate and distilled to give a residue, which, after crystallization from ethanol, gave 20 g. of I ($n = 6$, R = i-C_4H_9), m.p. 165–166°.

N,N'-Bis(p-carbethoxybenzoyl)hexamethylenediamine [I ($n = 6$; R = C_2H_5)]. e. *Phosphorus trichloride method.* Phosphorus trichloride (3.25 ml.) was added slowly to 4.3 g. of hexamethylenediamine in 20 ml. of pyridine held at 10°. After the reaction mixture was stirred for 0.5 hr. at 20°, a solution of 9.3 g. of p-carbethoxybenzoic acid in 25 ml. of warm pyridine was added. The reaction mixture was heated on the steam bath for 3 hr. after which time excess pyridine was distilled at reduced pressure. The residue was stirred sequentially with water, dilute sodium carbonate, and methanol to give 9.4 g. (82%) of I ($n = 6$, R = C_2H_5), m.p. 228–229°.

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[CONTRIBUTION FROM MELLON INSTITUTE]

Ozonolysis of Fluoranthene[1]

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During ozonolysis, a molecule of fluoranthene is attacked by two molecules of ozone. Using aqueous sodium bicarbonate to decompose the active-oxygen-containing products thus formed, fluorenone-1-aldehyde was obtained in high yield along with lesser amounts of fluorenone-1-carboxylic acid. Fluorenone-1-carboxylic acid was obtained in high yield by peracetic acid oxidation of fluorenone-1-aldehyde. A near quantitative yield of the dimethyl acetal of fluorenone-1-aldehyde was obtained by refluxing the aldehyde in methanol in the presence of a trace of peracetic acid. Alkaline cleavage of the dimethyl acetal of fluorenone-1-aldehyde produced the previously unreported isodiphenaldehydic acid in excellent yield. Good yields of isodiphenic acid were obtained by ozone oxidation of the aldehyde-acid. Baeyer-Villiger oxidation of fluorenone-1-carboxylic acid produced the previously unreported 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one. The n-butyl ester of this lactone was also prepared and characterized.

Fluoranthene (I) reportedly has been ozonized to a mixture of fluorenone-1-aldehyde (II) and fluorenone-1-carboxylic acid (III),[2–4] but the yield was only about 30%. In recent years, there have been many new developments concerning the reaction of ozone with organic compounds.[5] It seemed advisable, therefore, to re-evaluate the action of ozone on fluoranthene in the light of new reactions and techniques. By analogy with the ozonolysis of naphthalene,[6] one might expect that one mole of fluoranthene would react readily with two moles of ozone to give the difficultly accessible 1-substituted fluorenones in high yield. This was indeed found to be so. It should be mentioned that a recent publication by Copeland and co-workers[7] (which appeared after the completion of our work) agrees with our conclusions although the experimental approach was different. Copeland reports an 84% yield of II and an 80% yield of III from the ozonolysis of fluoranthene in an unspecified solvent.

When a suspension of fluoranthene in anhydrous t-butyl alcohol was treated with two molecular equivalents of ozone at room temperature, an orange-yellow solution resulted. Titration of the active oxygen showed that 93% of the theoretical was present in the solution. Furthermore, the active oxygen was present as hydroperoxide since a positive test was obtained using lead tetraacetate.[8] It was not hydrogen peroxide, however, because a negative test was obtained with a titanium salt. The distinguishing test is based on the yellow-orange color which is developed by titanic acid in the presence of hydrogen peroxide but which is not developed with other hydroperoxides.[9] Decomposition of the active-oxygen-containing solution by steam distillation resulted in an orange-yellow solid, which was a mixture of fluorenone-1-aldehyde (about 60%) and fluorenone-1-carboxylic acid (about 40%). In addition, the aqueous phase was found to contain glyoxal, hydrogen peroxide, and

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[1] Paper presented before the Division of Organic Chemistry, American Chemical Society, 136th Meeting, Atlantic City, N. J., Sept. 17, 1959.

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formic acid. Glyoxal was present only in a very small amount and was identified by the Ariyama color test,[10] which involves the formation of a deep blue color with arsenophosphotungstic acid solution. Formic acid was characterized by Duclaux values and estimated by titration. These facts are presumptive evidence for the reaction sequence as shown.

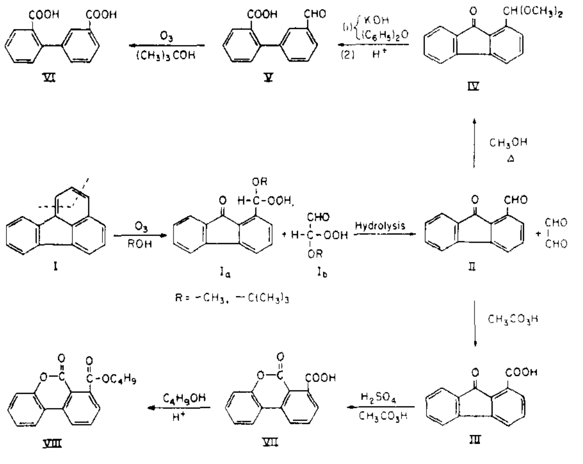
During the ozonolysis of fluoranthene in anhydrous *t*-butyl alcohol, the initial zwitterion intermediates react with the solvent to form fluorenone-1-*t*-butoxymethyl hydroperoxide (Ia) and *t*-butoxyformylmethyl hydroperoxide (Ib). Upon steam distilling, these two hydroperoxides are decomposed yielding fluorenone-1-aldehyde, glyoxal, hydrogen peroxide, and *t*-butyl alcohol. The hydrogen peroxide which is formed oxidizes most of the glyoxal to produce formic acid and part of the fluorenone-1-aldehyde to fluorenone-1-carboxylic acid. The hydrogen peroxide oxidation of glyoxal to formic acid has been reported in the literature.[11]

The highest yield of fluorenone-1-aldehyde was obtained by ozonolysis of fluoranthene in aqueous *t*-butyl alcohol. The intermediate was decomposed by the addition of aqueous sodium bicarbonate soution. The insoluble fluorenone-1-aldehyde precipitated and was removed by filtration. The yield was 77%. Distillation to remove the solvent, followed by acidification of the bicarbonate solution, produced fluorenone-1-carboxylic acid in 18% yield.

In methanol, ozonolysis takes the same course as in *t*-butyl alcohol but leads to some acetal formation. The acetal formation appears to be catalyzed by peroxides, and this will be more fully discussed later. The weakly basic sodium bicarbonate solution stabilizes the acetal, but acid hydrolysis results in the formation of the expected fluorenone-1-aldehyde. A typical run in methanol produced fluorenone-1-aldehyde in 36% yield, the dimethyl acetal of fluorenone-1-aldehyde in 25% yield, and fluorenone-1-carboxylic acid in 30% yield.

The reaction sequence which occurs when aqueous acetone is used as a solvent is not fully understood. It appears certain, however, that it is similar to the reaction in methanol or *t*-butyl alcohol since the same products are obtained. Aqueous acetone was actually the best solvent used since it dissolves fluoranthene more readily and thereby gives better ozone absorption. In a strictly commercial sense, it is also the cheapest of the solvents used. Using aqueous acetone, a 71% yield of fluorenone-1-aldehyde was obtained along with an 11% yield of fluorenone-1-carboxylic acid.

Since ozonolysis of fluoranthene affords the difficultly accessible 1-substituted fluorenones in good yield, some reactions of these materials were studied to determine their general utility in organic synthesis. Fluorenone-1-aldehyde has apparently never been prepared, except by ozonolysis of fluoranthene; whereas, fluorenone-1-carboxylic acid can be obtained from the parent hydrocarbon using the usual oxidants. The yields of carboxylic acid, however, were only of the order of 50%.[12]



Fluorenone-1-aldehyde undergoes some reactions characteristic of aromatic aldehydes readily; others only with difficulty or not at all. For example, attempts to oxidize fluorenone-1-aldehyde to the carboxylic acid with ozone were unsuccessful, and the maximum yield obtained in any solvent was 26%. Liquid-phase air oxidation was also unsuccessful, but oxidation with peracetic acid gave an 80% yield. The dimethyl acetal of fluorenone-1-aldehyde was formed in almost quantitative yield by refluxing the aldehyde in methanol in the presence of a catalytic amount of peracetic acid. Attempts to reduce the aldehyde to an alcohol by means of the crossed Cannizzaro reaction and catalytic hydrogenation were unsuccessful, and Meerwein-Pondorf-Verely reduction gave 1-hydroxymethyl-9-fluorenol as the major product.

In his study on the opening of the ketonic ring in substituted fluorenones, Huntress[13] subjected fluorenone-4-carboxylic acid to the action of potassium hydroxide in diphenyl ether and obtained both diphenic and 2-phenyl isophthalic acid. The reaction was not complete, however, and 15 to 25% of the original keto-acid was recovered from the mixture of fusion products. When fluorenone-1-carboxylic acid was subjected to the action of alkali in diphenyl ether, a single product, isodiphenic acid, was obtained in 61% yield. Here, too, reaction was not complete, and 12% of the original keto-acid was recovered unchanged.

A novel way of causing the reaction to go to completion was discovered. The keto-aldehyde (fluorenone-1-aldehyde) was converted into the dimethyl acetal. Alkaline cleavage of the dimethyl acetal proceeded smoothly and resulted in a 94% yield of the heretofore unreported isodiphenaldehydic acid.

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Ozone oxidation of this aldehyde-acid in *t*-butyl alcohol produced isodiphenic acid in 74% yield.

Baeyer-Villiger oxidation of fluorenone-1-carboxylic acid at room temperature with peracetic and sulfuric acids for two days produced a nearly quantitative yield of crude 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one, which melted with decomposition above 200°. A portion of this material was recrystallized to a constant melting point of 244–247°. Proof of structure was accomplished by saponifying the product with sodium hydroxide and oxidizing with potassium permanganate. Depending on whether the lactone is the 1- or 8-carboxy isomer, hemimellitic or phthalic acid would be the expected product. Hemimellitic acid was the only product obtained; therefore, the lactone is the one-isomer. The *n*-butyl ester of the carboxy-lactone was obtained in 58% yield by refluxing the crude oxidation product with *n*-butyl alcohol and *p*-toluenesulfonic acid for five hours while removing water. The purified ester melts at 140–142°.

EXPERIMENTAL

The fluoranthene used in this work was commercial material, m.p. 110°, and was estimated to be 98 to 99.5% purity. The methanol, *t*-butyl alcohol, and acetone were reagent-grade materials. All melting points are uncorrected.

The ozonator used in this research was a Welsbach Corporation Model T-23 laboratory ozonator operated with 115 volt, 60 cycle current and using pure, clean, dry oxygen. The oxygen feed was obtained in commercial cylinders and dried to at least −60°F. dew point with a laboratory "Lectrodryer" sold by the Pittsburgh Lectrodryer Corporation. The reaction vessels were the usual gas-absorption type with the gas inlet at the bottom, a coarse-porosity sealed-in fritted disk just above the inlet to disperse the incoming gases, and the outlet at the top. The reaction vessel was equipped with a mechanical or magnetic stirring device and a reflux condenser to return solvent from the gas stream. Ozone concentrations were determined with a Welsbach Model C ozone meter or iodometrically as detailed in the *Welsbach Basic Manual of Applications and Laboratory Ozonization Techniques*.

I. Ozonizations. A. Ozonolysis of fluoranthene in anhydrous t-butyl alcohol to give fluorenone-1-aldehyde (II). A suspension of fluoranthene (10.0 g., 0.0495 mole) in 200 ml. of anhydrous *t*-butyl alcohol was treated with approximately 2.3 weight per cent ozone (in oxygen) at room temperature and a flow rate of 102 l. per hr. for 96 min. Using these conditions, 4.96 g. (0.103 mole) of ozone (2.08 molecular equivalents) was passed into the reaction mixture. The resulting yellow-orange solution was transferred into a 250-ml. volumetric flask and diluted to the mark with *t*-butyl alcohol. A 10-ml. aliquot was titrated for active oxygen. The total solution was found to contain 92.5 mmoles of active oxygen (theory = 99 mmoles). The solution gave a positive test for hydroperoxide with lead tetraacetate[8] and a negative test for hydrogen peroxide using titanous chloride solution.[9] The *t*-butyl alcohol was removed by steam distillation, and the residue which remained in the flask was removed by filtration yielding 9.9 g. of orange solids which melted at 152–162°. The aqueous filtrate gave the Ariyama[10] color test for glyoxal and a positive test for hydrogen peroxide.[9] The aqueous filtrate also contained formic acid, which was characterized by Duclaux values. The orange solids from above were allowed to reflux for 1 hr. with 200 ml. of 7% aqueous sodium bicarbonate solution. Filtration yielded 6.6 g. (64% yield) of crude fluorenone-1-aldehyde, which melted at 169–175°. Several recrystallizations from ethanol raised the melting point to 193–194°.[4] Upon acidification of the bicarbonate solution, precipitation occurred. Filtration yielded 3.3 g. (30% yield) of crude fluorenone-1-carboxylic acid, which melted at 175–183°. Several recrystallizations from glacial acetic acid raised the melting point to 196–197°.[4]

B. Ozonolysis of fluoranthene in aqueous t-butyl alcohol to give fluorenone-1-aldehyde (II). A suspension of fluoranthene (10.0 g., 0.0495 mole) in 200 ml. of 87.5% aqueous *t*-butyl alcohol was treated with approximately 2.0 weight per cent ozone (in oxygen) at room temperature (30°) and a flow rate of 102 l. per hr. for 2 hr. and 33 min. Under these conditions, 6.63 g. (0.138 mole) of ozone or 2.8 molecular equivalents were passed into the reaction mixture. The ozone absorption was poor and only about 2 molecular equivalents of ozone was actually absorbed. After flushing with oxygen, the light-yellow solution was transferred into an 800-ml. beaker containing 300 ml. of 5% aqueous sodium bicarbonate solution. Precipitation occurred, and the yellow solid was removed by filtration yielding 6.1 g. (59.2% yield) of fluorenone-1-aldehyde which melted at 188–191°. Recrystallization raised the melting point to 193–194°; lit.,[4] m.p. 194°. The filtrate was distilled to remove *t*-butyl alcohol. Filtration yielded an additional 1.9 g. (18.4% yield) of crude fluorenone-1-aldehyde, which melted at 145–158° (identified by infrared spectrum). Upon acidification of the remaining bicarbonate solution, precipitation occurred. Filtration yielded 2.0 g. (18% yield) of crude fluorenone-1-carboxylic acid as an orange solid which melted at 170–181°. Recrystallization from glacial acetic acid raised the melting point to 196–197°; lit.,[4] m.p. 197°.

C. Ozonolysis of fluoranthene in methanol. A solution of fluoranthene (10 g., 0.0495 mole) in 400 ml. of methanol was treated with approximately 4.3 weight per cent ozone (in oxygen) at a flow rate of 34 l. per hr. at room temperature (30°) for 2 hr. and 36 min. Under these conditions, 2.08 molecular equivalents (4.95 g., 0.103 mole) of ozone was passed into the reaction mixture. After flushing with oxygen, the light-yellow solution was transferred into a 1-l. flask, and a mixture of 200 ml. of 7% aqueous sodium bicarbonate solution and 200 ml. of water was added. The methanol was then removed by distillation to a head temperature of 95°. A brown viscous oil remained in the bicarbonate solution and was extracted using 100 ml. of chloroform. The chloroform was evaporated to dryness and the residue treated with aqueous acetone (100:50) and concd. hydrochloric acid (2 ml.). Upon refluxing, a precipitate formed yielding 3.7 g. (35.9% yield) of crude fluorenone-1-aldehyde which melted at 188–192°. A mixed melting point with an authentic sample showed no depression. Evaporation of the aqueous acetone yielded 3.3 g. (25% yield) of crude dimethyl acetal of fluorenone-1-aldehyde (identified by its infrared spectrum). Acidification of the bicarbonate solution yielded 3.3 g. (29.7% yield) of crude fluorenone-1-carboxylic acid which melted at 185–190° (no depression with an authentic sample).

D. Ozonolysis of fluoranthene in aqueous acetone. A suspension of fluoranthene (60 g., 0.297 mole) in a mixture of acetone (800 ml.) and water (400 ml.) was treated with approximately 3.8 weight per cent ozone (in oxygen) at a flow rate of 102 l. per hr. at room temperature (30°) for 5 hr. and 55 min. Under these conditions, 2.08 molecular equivalents (30.3 g., 0.62 mole) of ozone was passed into the reaction mixture. After flushing with oxygen, the light-yellow solution was transferred into a 4-l. beaker and 1200 ml. of 7% aqueous sodium bicarbonate solution added. Precipitation occurred, and the yellow solid was removed by filtration, washed with water, and dried yielding 44.2 g. (71.4% yield) of crude fluorenone-1-aldehyde which melted at 187–191°. Recrystallization from ethanol raised the melting point to 193–194°; lit.,[4] m.p. 194°. The filtrate was distilled to remove the acetone and then acidified with concd. hydrochloric acid. An orange solid precipitated and was removed by filtration yielding 7.2 g. (10.8% yield) of crude fluorenone-1-carboxylic acid which melted at 177–185°. Recrystallization from glacial acetic acid raised the melting point to 196–197°; lit.,[4] m.p. 197°.

II. *Reactions involving the ozonolysis products of fluoranthene. A. Preparation of fluorenone-1-carboxylic acid* (III). A mixture of crude fluorenone-1-aldehyde (10.4 g., 0.05 mole), glacial acetic acid (100 ml.), and Becco 40% peracetic acid (10 ml., 0.06 mole) was placed in a 500 ml. three-neck flask equipped with a mechanical stirrer and reflux condenser. Heat was supplied using a heating mantle, and the mixture was allowed to reflux for 3 hr. The mixture was transferred into a 400-ml. beaker and an equal volume of water added. Precipitation occurred, and the product was removed by filtration, washed with water, and dried yielding 9.8 g. (87.5% yield) of fluorenone-1-carboxylic acid which melted at 181–189°. Recrystallization from glacial acetic acid raised the melting point to 197°.[4]

B. Preparation of the dimethyl acetal of fluorenone-1-aldehyde (IV). Recrystallized fluorenone-1-aldehyde (10 g., 0.048 mole), methanol (500 ml.), and Becco 40% peracetic acid (1 ml.) were placed in a 1-l. round-bottom flask. The flask was fitted with a reflux condenser and the mixture allowed to reflux for about 12 hr. (overnight). The fluorenone-1-aldehyde went into solution after about 10 min. After refluxing, a mixture of aqueous 7% sodium bicarbonate solution (50 ml.) and water (50 ml.) was added to the mixture and the methanol removed by distilling to a head temperature of 95°. Upon cooling, the yellow oil present in the aqueous residue solidified. Filtration yielded 12.0 g. (98.4% yield) of the dimethyl acetal of fluorenone-1-aldehyde, which melted at 81–82°. Recrystallization from *n*-heptane raised the melting point to 82–83°.

Anal. Calcd. for $C_{16}H_{14}O_3$: C, 75.60; H, 5.52; methoxyl, 24.40. Found: C, 75.84; H, 5.76; methoxyl, 23.88.

C. Preparation of isodiphenaldehydic acid (V). A solution of the dimethyl acetal of fluorenone-1-aldehyde (5.0 g., 0.0197 mole) in diphenyl ether (120 ml.) was placed in a 500-ml. three-neck flask which had been fitted with a condenser, stirring device, and a thermometer. Solid potassium hydroxide (16.0 g., 0.286 mole) was added and the flask heated to 160° using a heating mantle. The mixture was stirred vigorously during the heating, and the potassium hydroxide gradually went into solution. The reaction was allowed to proceed for 2 hr. at a temperature of 160–175°. After completion of the cleavage reaction, the mixture was cooled and stirred with about one half its volume of water until both resultant salts and excess alkali were dissolved. The two layers were then separated and the diphenyl ether layer further extracted with water. The combined aqueous fractions were filtered. From the pale-yellow filtrate, insoluble acids were precipitated by acidification with concd. hydrochloric acid. The light-yellow product was removed by filtration, washed with water, and dried yielding 4.2 g. (94.3% yield) of crude isodiphenaldehydic acid melting at 104–106°. Recrystallization from an ethyl acetate–*n*-heptane mixture raised the melting point to 110–111.5°.

Anal. Calcd. for $C_{14}H_{10}O_3$: C, 74.33; H, 4.46; neut. equiv., 226. Found: C, 73.76; H, 4.51; neut. equiv., 218.

D. Preparation of isodiphenic acid (VI). A solution of the crude isodiphenaldehydic acid from the previous reaction (2.26 g., 0.01 mole) in anhydrous *t*-butyl alcohol (100 ml.) was treated with approximately 3 weight per cent ozone (in oxygen) at a flow rate of 34 l. per hr. at room temperature (30°) for 1 hr. Under these conditions, 1.4 molecular equivalents (0.67 g., 0.014 mole) of ozone was passed into the solution. After ozonization, the colorless solution was poured into a 500-ml. flask which contained 100 ml. of 7% aqueous sodium bicarbonate solution, and the *t*-butyl alcohol was removed by distillation to a head temperature of 95°. Upon acidification of the remaining bicarbonate solution with hydrochloric acid, precipitation occurred yielding 1.8 g. (74% yield) of isodiphenic acid which melted at 219–221°. The reported melting point for isodiphenic acid is 216°.[14]

Neut. equiv. Calcd.: 121.0. Found: 120.2.

E. Preparation of 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one (VII). A mixture of recrystallized fluorenone-1-carboxylic acid (15.7 g., 0.07 mole), glacial acetic acid (100 ml.), and Becco 40% peracetic acid (17.5 ml., 0.11 mole) was placed in a 250-ml. Erlenmeyer flask and the mixture cooled in an ice bath to 0°. Concd. sulfuric acid (20 ml., 0.375 mole) was added slowly and the mixture stirred with a magnetic stirrer. The reaction was then allowed to proceed at room temperature for 72 hr. The glacial acetic acid was removed in a flash evaporator and the sulfuric acid carefully neutralized with a solution of sodium hydroxide (26 g.) in 260 ml. of water. Precipitation occurred, and the product was removed by filtration, washed with water, and dried yielding 16.2 g. (96.5% yield) of crude 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one which melted at 214–231° dec. An analytical sample was prepared by repeated recrystallization (ethyl acetate), which raised the melting point to 244–247°. Proof of structure was accomplished by alkaline permanganate oxidation to yield hemimellitic acid, demonstrating that this compound was the 1- rather than the 8-carboxy isomer.

Anal. Calcd. for $C_{14}H_8O_4$: C, 70.0; H, 3.36; neut. equiv., 240. Found: C, 70.49; H, 3.65; neut. equiv., 247.

F. Preparation of the n-butyl ester of 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one (VIII). A mixture of crude 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one (9.3 g., 0.0388 mole), *n*-butyl alcohol (100 ml.), toluene (100 ml.), and *p*-toluenesulfonic acid hydrate (5 g.) was placed in a 500-ml. round bottom flask which was fitted with a reflux condenser and Dean Stark trap. The mixture was allowed to reflux until the theoretical amount of water had collected in the trap (5 hr.). After cooling, the solution was washed with 7% aqueous sodium bicarbonate (100 ml.) and twice with water (50 ml.). The solution was concentrated to a volume of about 50 ml. by evaporation, and the resulting precipitate was removed by filtration yielding 6.6 g. (57.8% yield) of crude *n*-butyl ester of 1-carboxy-9-oxa-9,10-dihydrophenanthrene-10-one which melted at 139–142°. Recrystallization of a portion from ethyl acetate raised the melting point to 140–142°. The purified product had a saponification equivalent of 149 (theoretical = 148).

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PITTSBURGH 13, PA.

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