

posed to sunlight for four days (March). The yellowish-brown deposit formed was filtered off and recrystallized from benzene in orange crystals, m.p. about 228° dec. (dark brown melt), yield 0.3 g. The compound gave green color with concentrated sulfuric acid. It was difficultly soluble in glacial acetic acid but went easily into sodium hydroxide solution (10%) and in sodium carbonate solution at room temperature (red color) and was recovered unchanged from the latter solution by acidification. V gave in alcoholic solution, a deep green color with ferric chloride, which on addition of small quantities of aqueous ammonia or aqueous sodium carbonate solution turned reddish-brown. V gave a deep red color with titanous chloride and V sublimes in vacuum.

Anal. Calcd. for $C_{13}H_9O_3N$: C, 68.7; H, 3.9; N, 6.2; active H, 0.9 (for 2 H). Found: C, 68.8; H, 3.9; N, 6.1; active H, 1.1.

Oxidation of V to Phthalic Anhydride.—Five-tenths gram of V, 0.3 g. of mercuric sulfate and 4 ml. of concentrated sulfuric acid were placed in a glass retort (100-ml. capacity). The mixture was then heated in a metal-bath for 10 minutes at 250° (bath temperature), then for 50 minutes at 300–310° (bath temperature), when colorless needles were observed on the colder part of the retort tube. The crystals were scratched out of the tube and sublimed to give the characteristic needles of phthalic anhydride (m.p. and mixed m.p. determination and positive fluorescein test).

Action of Hydrochloric Acid on V.—One-tenth gram of V and 10 ml. of dilute hydrochloric acid (1:1) were refluxed for 15 minutes. The mixture was allowed to cool and made alkaline with sodium hydroxide in presence of ice, when no evolution of ammonia was observed (HCl test).

Action of *o*-Phenylenediamine on V.—Fifteen-hundredths gram of V and 0.1 g. of *o*-phenylenediamine were dissolved in the necessary amount of glacial acetic acid at 30° and maintained at this temperature for a half-hour. The mixture then was poured into ice-cold water (600 ml.) and left to stand for one hour. The orange deposit formed was filtered off and proved to be V; the m.p. was undepressed on admixture with an authentic specimen; both samples gave the same ferric chloride reaction (green), the same titanous chloride reaction (deep red), the same color with aqueous sodium carbonate solution and the same shape and color of crystals (from benzene).

The same experiment was carried out at 60° and similar results were obtained.

1,2-Diacetoxy-3-aceto-4-cyanonaphthalene.—Two-tenths gram of V and 6 ml. of acetic anhydride were refluxed for one hour, poured on ice and left overnight. The deposit formed was filtered off and recrystallized from methyl alcohol in almost colorless crystals, m.p. 160° (deep reddish-brown melt), yield almost quantitative, not soluble in sodium

hydroxide solution (10%) but soluble in alcohol giving a yellowish solution.

Anal. Calcd. for $C_{17}H_{13}O_5N$: C, 65.6; H, 4.2; N, 4.5. Found: C, 65.6; H, 4.3; N, 4.7.

1,2-Dihydroxy-3-propiono-4-cyanonaphthalene (V replace $COCH_3$ by COC_2H_5).—One gram of propionaldehyde and 1 g. of I in 30 ml. of benzene were exposed to sunlight for a fortnight (May–June). There was no deposit; the solution was concentrated under reduced pressure and cooled in ice. The orange deposit formed was filtered off and recrystallized from benzene in orange crystals, m.p. 168°, yield 0.22 g. The substance gave a green color with concentrated sulfuric acid.

Anal. Calcd. for $C_{14}H_{11}O_3N$: C, 69.7; H, 4.6; N, 5.8; mol. wt., 241. Found: C, 69.6; H, 4.9; N, 5.6; mol. wt. (Rast), 229.

1,2-Dihydroxy-4-cyanonaphthalene from 4-Cyano-1,2-naphthoquinone.—Five-tenths gram of 4-cyano-1,2-naphthoquinone was powdered and suspended in 5 ml. of alcohol. A saturated solution of sodium hydrosulfite ($Na_2S_2O_4$) (room temperature) was added dropwise with shaking. Addition was continued till the color became very faint, when a pale brown deposit separated out. A small volume of water was added and the mixture warmed till the solid dissolved; it was filtered while hot and left to cool. The product that separated was filtered and recrystallized from dilute alcohol in colorless crystals, m.p. 208° (yield almost quantitative), undepressed on admixture with an authentic specimen.¹³

1,2-Diacetoxy-4-cyanonaphthalene.—Two-tenths gram of 1,2-dihydroxy-4-cyanonaphthalene and 3 ml. of acetic anhydride were refluxed for one hour, poured on ice and left for a few hours. The product obtained was triturated well, filtered off and recrystallized from methyl alcohol in colorless crystals, m.p. 152° (yield almost quantitative). It gave no color with concentrated sulfuric acid and was insoluble in sodium hydroxide solution (10%).

Anal. Calcd. for $C_{13}H_{11}O_4N$: C, 66.9; H, 4.1; N, 5.2; acetyl group, 32.0 (for 2). Found: C, 67.0; H, 4.2; N, 5.4; acetyl group, 31.8.

Hydrolysis of 1,2-Diacetoxy-4-cyanonaphthalene.—One-tenth gram of 1,2-diacetoxy-4-cyanonaphthalene, 6 ml. of concentrated hydrochloric acid and 4 ml. of ethyl alcohol were refluxed for three hr. on a sand-bath, cooled and diluted with water. The colorless crystals formed (yield 0.05 g.) were filtered off and proved to be 1,2-dihydroxy-4-cyanonaphthalene by m.p. and mixed m.p. determinations. Both samples gave the same reaction with ferric chloride (green color).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

The Structure of Anthracene Photodimers

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RECEIVED FEBRUARY 7, 1955

The products resulting from the irradiation by sunlight of several 9-substituted anthracene derivatives (formyl, carbomethoxy, hydroxymethyl) have been shown to be dimers composed of two anthracene units bonded together at the 9,9'- and 10,10'-positions. The head-to-head structure I for these products has been established by the unambiguous synthesis of a compound possessing structure I via the intramolecular cyclization of 9-anthracene anhydride.

Introduction

The conversion of anthracene and anthracene derivatives to higher melting compounds by the action of sunlight has been known since 1866 when Fritzsche isolated dianthracene from irradiation of a benzene solution of anthracene.¹ Many other photomerides have been reported, derived from anthracenes substituted at the 1-position (methyl,²

chloro,² carboxy³), the 2-position (methyl,⁴ carboxy³), the 1,4-positions (chloromethyl²), the 1,9-positions (chlorobromo²) and the 9-position (bromo,^{2,5} carboxy,³ methyl,⁶ ethyl,⁶ formyl⁷ and

(3) F. Weigert and L. Kummerer, *Chem. Ber.*, **47**, 898 (1914).

(4) W. R. Orndorff and H. A. Megraw, *Am. Chem. J.*, **22**, 152 (1899).

(5) H. Meyer and A. Eckert, *Monatsh.*, **39**, 241 (1918).

(6) A. Willemart, *Compt. rend.*, **205**, 993 (1937).

(7) P. D. Bartlett and F. D. Greene, *THIS JOURNAL*, **76**, 1088 (1954).

(1) J. Fritzsche, *J. prakt. Chem.*, **101**, 333 (1867).

(2) O. Fischer and H. Ziegler, *ibid.*, [2] **86**, 289 (1912).

carbomethoxy⁷). Compounds involving substitution at both the 9- and 10-positions were unaffected by sunlight.⁶

The dimeric nature of these products has been established by ebullioscopic^{3,4,8} and cryoscopic methods.⁹ The results of a detailed study of dianthracene by electron diffraction¹⁰ and crystal structure analysis⁸ were consistent with a formulation of the dimer as a structure composed of two anthracene units bonded at the 9,9'- and 10,10'-positions. The present paper provides chemical evidence establishing this structure for the dimers of several 9-substituted anthracenes.

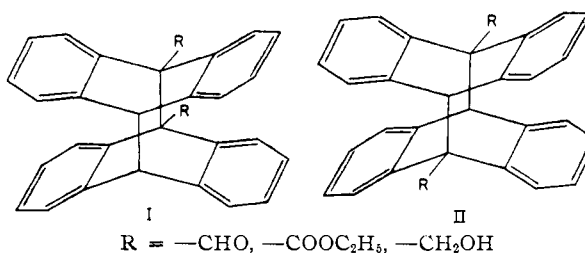
Discussion

Preparation of the Dimers.—Exposure to sunlight of a solution of the colored monomers in an inert solvent resulted in the slow precipitation of colorless material. For a particular derivative, the dimerization proceeded with roughly equal facility in a variety of solvents (benzene, chloroform, acetic acid and ethanol) although considerable variation was noted in the ease of dimerization of the different compounds. The following sequence is in the order of increasing ease of dimerization: 9-hydroxymethyl, 9-formyl, 9-carbomethoxy, 9-anthroic anhydride.¹¹ The anhydride, as expected, was the most rapid (by virtue of its intramolecular character). The reactions initially were run in quartz flasks, but investigations with the 9-formyl compound showed that the reaction proceeded equally well in Pyrex or soft glass vessels, an observation that may be applicable to the other compounds in this series.

All of the photomerides that have been investigated are colorless compounds of higher melting point and lower solubility in the common solvents than the corresponding monomers. At the melting point, these compounds are quantitatively dissociated to the monomers.

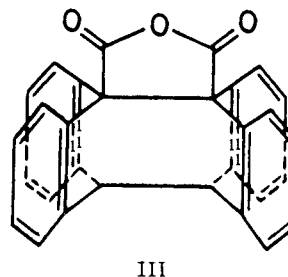
Structure.—A strong indication of the structure of the irradiation products of 9-substituted anthracene derivatives is provided by the infrared absorption spectra. The 6.0 μ conjugated carbonyl band of 9-anthraldehyde is shifted to 5.8 μ in the dimer, characteristic of an unconjugated carbonyl group. The 6.9 μ band in the carbon-hydrogen bending region which is observed as a single band in the 9-formyl, 9-hydroxymethyl derivatives and in 9-anthroic anhydride is replaced by two bands at 6.78 and 6.88 μ in the photomerides (possibly due to a change in the nature of the C-10 carbon hydrogen bond). The two bands at 6.9 and 6.98 μ in 9-methyl anthroate are replaced by three bands, at 6.78, 6.88 and 6.98 μ . These observations are suggestive of a structure similar to that proposed for dianthracene, namely, two monomeric units bonded together at the 9,9'- and 10,10'-positions. However, with 9-substituted dimers, two such

structures are possible: a head-to-head structure, I, and a head-to-tail structure, II.



In order to distinguish between I and II, an unambiguous synthesis of a compound possessing structure I was undertaken.

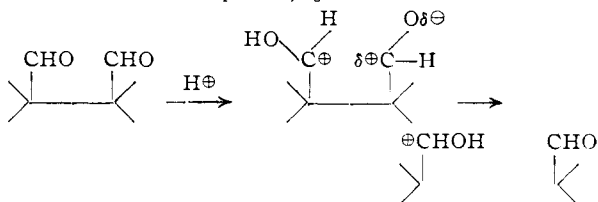
9-Anthroic anhydride was prepared by the action of ketene on 9-anthroic acid and subsequent pyrolysis of the mixed anhydride. The infrared spectrum of 9-anthroic anhydride shows the two bands characteristic of a conjugated anhydride at 5.6 and 5.8 μ . Irradiation of a solution of the anhydride in chloroform converted the yellow anhydride into a colorless anhydride, III, whose infrared absorption spectrum exhibited a small band at 5.4 μ , a strong band at 5.6 μ and a strong band at 8.08 μ , characteristic of a five-membered cyclic anhydride. Reduction of this compound by an ethereal solution of lithium aluminum hydride



gave predominantly the monomeric 9-hydroxymethylanthracene, accompanied by a small amount (10% yield) of dimeric 9-hydroxymethylanthracene (bis-9-hydroxymethylanthracene (I, R = CH₂OH)).¹²

That the material was formed by the direct reduction of the cyclic anhydride and not by the dimerization of 9-hydroxymethylanthracene was shown by a control experiment in which 9-hydroxymethylanthracene, subjected to the reduction conditions, was recovered in quantitative yield. Reduction of bis-9-anthraldehyde and bis-9-methyl anthroate with ethereal lithium aluminum hydride gave bis-9-hydroxymethylanthracene. The bis-

(12) The facile formation of 9-hydroxymethylanthracene upon treatment of the cyclic anhydride with lithium aluminum hydride is paralleled by the ready acid-catalyzed dissociation of bis-9-anthraldehyde and bis-9-methyl anthroate. We believe that these cleavages are due to electrostatic repulsions, e.g.



Further work on this cleavage is in progress.

(8) W. R. Orndorff and F. K. Cameron, *Am. Chem. J.*, **17**, 658 (1895).

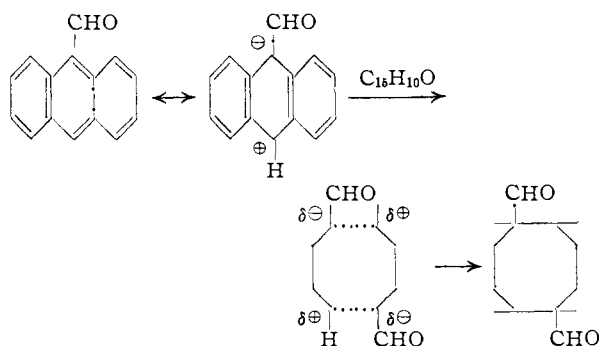
(9) K. Eibs, *J. Prakt. Chem.*, [2], **44**, 467 (1891).

(10) J. Hengstenberg and J. Palacios, *Anales real soc. espan. fis. y quim. (Madrid)*, **30**, 5 (1932).

(11) C. Dufraisse and M. Gerard, *Bull. soc. chim. France*, [5] **4**, 2052 (1937), have reported that chloroform and carbon disulfide inhibited the photodimerization of anthracene while ether promoted it.

9-hydroxymethylanthracene prepared by irradiation of 9-hydroxymethylanthracene was identical with that prepared by reduction of bis-9-anthraldehyde and bis-9-methyl anthroate, as shown by the superimposability of the infrared spectra and identity of melting point and mixed melting point. Furthermore, the same criteria showed that the bis-9-hydroxymethylanthracene, prepared by reduction of the cyclic anhydride, was identical with the material produced by reduction of aldehyde and ester dimers and by irradiation of the hydroxymethyl compound. This evidence shows that these photomerides are all head-to-head dimers, I.

Mechanism of Formation.—The mechanism of formation of dianthracene from anthracene has been investigated extensively.¹³ The rate of appearance of dianthracene is independent of anthracene concentration between the limits of 6.5 and 17 millimolar in toluene. This is compatible with a process in which an anthracene molecule is excited (wave length used, 366 m μ) to an activated state, followed by bimolecular reaction between the excited molecule and a normal anthracene molecule. The excited molecules are consumed in effective collisions with normal anthracene molecules to form dimer, and in deactivating collisions with normal anthracene molecules, and *not* by deactivating collisions with solvent molecules. (Dependence of rate on anthracene concentration at lower concentrations is presumably due to the importance of the latter term under those conditions.¹³) Consideration of the activated state of anthracene as a diradical has appeared in varying degrees of precision from the earliest work onward.¹⁴⁻¹⁶ The formation of dimers of 9-substituted anthracene compounds by irradiation also may proceed by reaction of an activated molecule with a normal molecule. The radical nature of the reaction is adduced by the photochemical activation and by the head-to-head structure of the dimer. A polar process would be expected to give head-to-tail products.



The independence of the reaction rate on solvent and the concomitant oxidation to yield anthraquinone are also in accord with a radical reaction. (This side reaction becomes increasingly important as the photolysis proceeds. Anthraquinone formation may be appreciable in the photolysis of

anthracene¹⁷ and of anthraldehyde.¹⁸ Dimerization in the absence of oxygen eliminates this side reaction.)

The head-to-head structure of the dimer is reminiscent of a number of thermal and photolytic processes. Thermal treatment of chloroprene affords (among other products) 1,6-dichloro-1,5-cyclooctadiene.¹⁹ Acrylonitrile has been converted thermally into 1,2-dicyanocyclobutane in low yield.²⁰ Diels-Alder adducts are "head-to-head" structures in many cases, *e.g.*, 1-phenyl-1,3-butadiene and acrolein yield only 2-phenyl-3-cyclohexenecarboxaldehyde.²¹ Although dimerizations of several types of compounds (primarily of quinones, α,β -unsaturated carbonyl compounds, anthracenes and 1- and 2-azaanthracenes) have been effected by sunlight,²² the stereochemistry of the products has been proved in only a few cases. Furthermore, it is important to differentiate between irradiation of solutions of compounds and of the compounds in the crystalline state. In the latter case, both head-to-head and head-to-tail products are often obtained, as is the case with irradiation of cinnamic and allocinnamic acid. The production of both head-to-head and head-to-tail dimers is here a reflection of the arrangement of molecules in the crystal rather than of the comparative energy levels of different transition states. In particular, irradiation of crystalline benzalacetophenone affords both truxinic and truxillic-type products whereas irradiation of the material in solution affords only the truxinic-type product (head-to-head structure). A number of other photolytic processes also yield "head-to-head" structures.²³ The formation of head-to-head products is compatible with a process in which the positions of less stability as radicals are first coupled followed by the coupling of the positions of greater radical stability.²⁴

Experimental²⁵

9-Anthraldehyde was prepared by the method of Fieser, Hartwell and Jones.²⁶ The ultraviolet spectrum has absorption peaks at 233 m μ (ϵ_{max} , 42,000) and 263 m μ (ϵ_{max} , 77,000); the infrared spectrum shows absorption in the carbonyl region at 6.00 μ .

9-Anthroic acid was prepared by the method of Latham, May and Mosettig.²⁷

(17) S. S. Bhatnagar, P. L. Kapur and G. Kaur, *Proc. Indian Acad. Sci.*, **10A**, 468 (1939).

(18) We have little information on this oxidation; formation of anthraquinone may occur through the peracid or possibly *via* a light-induced decarbonylation.

(19) A. C. Cope and W. R. Schmitz, *THIS JOURNAL*, **72**, 3056 (1950).

(20) E. C. Coyner and W. S. Hillman, *ibid.*, **71**, 324 (1949).

(21) E. Lehmann and W. Paasche, *Chem. Ber.*, **68**, 1146 (1935).

(22) For a recent review, see Ahmed Mustafa, *Chem. Revs.*, **51**, 1 (1952).

(23) G. Büchi, C. G. Inman and E. S. Lipinsky, *THIS JOURNAL*, **76**, 4327 (1954).

(24) For a discussion of this process with reference to the formation of trimethylene oxides by irradiation of an aldehyde-olefin mixture, see reference 23.

(25) Melting points are corrected. We are indebted to S. M. Nagy and his associates for analyses and infrared spectra, which were recorded with a Baird double beam infrared recording spectrophotometer equipped with a sodium chloride prism.

(26) L. F. Fieser, J. L. Hartwell and J. E. Jones, *Org. Syntheses*, **20**, 11 (1940).

(27) G. Latham, Jr., E. L. May and E. Mosettig, *THIS JOURNAL*, **70**, 1079 (1948).

(13) See M. Suzuki, *Bull. Chem. Soc. Japan*, **18**, 146 (1943); **22**, 172 (1949); **23**, 120 (1950), and earlier references cited therein.

(14) C. E. Linebarger, *Am. Chem. J.*, **14**, 597 (1892).

(15) E. Clar, *Chem. Ber.*, **65**, 503 (1932).

(16) A. Schönberg, *Trans. Faraday Soc.*, **32**, 514 (1936).

9-Methyl anthroate was prepared from the acid and diazomethane.⁷ Recrystallization from methanol gave material melting at 112–113°. The ultraviolet spectrum has an absorption peak at 253 m μ (ϵ_{\max} , 185,000) and a shoulder at 245 m μ (ϵ_{\max} , 100,000).

9-Hydroxymethylanthracene.—A 3-g. sample of 9-anthraldehyde was added in portions to a slurry of 0.7 g. of lithium aluminum hydride in 150 ml. of ether. After decomposition of the excess reductant with ethyl acetate the reaction mixture was added to 200 ml. of ice-cold 5% sulfuric acid. The product was taken up in ether, dried over magnesium sulfate, filtered, and the ether was removed under nitrogen (the product is readily oxidized in the air) yielding 2 g. of pale yellow material. Four recrystallizations from benzene gave long colorless needles, m.p. 154–155°.

Anal. Calcd. for C₁₆H₁₂O: C, 86.51; H, 5.81. Found: C, 86.20; H, 5.84.

9-Anthroic Anhydride.—This compound was prepared by the reaction of either ketene or acetic anhydride on 9-anthroic acid.

(A) **By Ketene.**—Ketene gas (*ca.* 0.3 mole) was bubbled through a solution of 10 g. (0.05 mole) of 9-anthroic acid in 500 ml. of anhydrous ether. Removal of the ether left a brown oil which solidified on cooling, m.p. 65–69°. The mixed anhydride was heated at 110° (0.5 mm.) for 24 hours, yielding 7 g. (70%) of dark yellow powder, m.p. 245–249°. Two recrystallizations from chloroform gave yellow prisms, m.p. 249–250°. The infrared spectrum shows characteristic anhydride bands at 5.6 and 5.8 μ .

Anal. Calcd. for C₂₀H₁₈O₃: C, 84.49; H, 4.26. Found: C, 84.23; H, 4.40.

(B) **From Acetic Anhydride.**—A solution of 5 g. of 9-anthroic acid in 80 ml. of acetic anhydride was heated under reflux for 6 hours. At 2-hour intervals 15 ml. of solvent was removed by distillation through a 20-cm. Vigreux column. The remainder of the solvent was removed under reduced pressure leaving an oily residue that solidified to a yellow crystalline mass. Three recrystallizations from cyclohexane afforded small yellow crystals, m.p. 85–86°, of the mixed anhydride of acetic acid and 9-anthroic acid. The crude mixed anhydride was converted in subsequent runs to 9-anthroic anhydride as described under procedure A.

Anal. Calcd. for C₁₇H₁₂O₃: C, 77.26; H, 4.58. Found: C, 77.25; H, 4.59.

Photodimer of 9-Anthraldehyde.—The procedure of Bartlett and Greene⁷ was modified as follows. Exposure of a solution of 4 g. of 9-anthraldehyde in 100 ml. of glacial acetic acid in a Pyrex flask to sunlight for one day resulted in a precipitate of white powder and yellow needles, 3.6 g. Washing of the precipitate with benzene effected the removal of the yellow material which was subsequently identified as anthraquinone; mixed m.p. with an authentic sample, 285–286°. Recrystallization of the white powder from benzene afforded large colorless cubic crystals, m.p. 186–187°. The melt on cooling resolidified to 9-anthraldehyde, melting at 104–105°. The infrared spectrum shows a sharp band at 5.8 μ .

Photodimer of 9-Hydroxymethylanthracene.—A solution of 2 g. of 9-hydroxymethylanthracene in 100 ml. of absolute ethanol in a quartz flask was exposed to sunlight for 2 days, giving a precipitate of white powder and anthraquinone, from which was isolated 200 mg. of colorless material melt-

ing at 257–260°. Three recrystallizations from pyridine yielded finely divided white powder, m.p. 269–270°. The infrared spectrum shows a broad band at 3.13 μ , suggestive of hydrogen bonding. The material gave analyses corresponding to the hemihydrate, even after 16 hours of drying at a temperature of 100° and a pressure of 0.1 mm.

Anal. Calcd. for C₂₀H₂₄O₂· $\frac{1}{2}$ H₂O: C, 84.67; H, 5.92. Found: C, 85.01, 84.35, 84.21; H, 5.86, 5.77, 5.91.

Photomeride of 9-Anthroic Anhydride (III).—A solution of 7 g. of 9-anthroic anhydride in 400 ml. of chloroform in a Pyrex flask was exposed to sunlight. Large colorless cubic crystals separated in an analytically pure condition soon after exposure. At 24-hour intervals crystals that had formed were separated by filtration and the filtrate was replaced in the sunlight: total yield 4.75 g. (68%), m.p. 279–281°. The melt on cooling resolidified to give 9-anthroic anhydride, m.p. 249–250°. 9-Anthroic anhydride was recovered quantitatively from an experiment in which it was heated under reflux in chloroform for 72 hours. The infrared spectrum of the photomeride shows the anhydride bands at 5.42 and 5.62 μ (the stronger of the two) and a band at 8.08 μ .

Anal. Calcd. for C₃₀H₁₈O₃: C, 84.49; H, 4.26. Found: C, 84.69; H, 4.20.

Reduction of Photodimers.—The photodimers of 9-anthraldehyde and 9-methyl anthroate were reduced by the following method. To a slurry of 3.04 g. (0.08 mole) of lithium aluminum hydride in 300 ml. of ether was added 1.32 g. (0.0032 mole) of bis-9-anthraldehyde, and the mixture was heated under reflux for 48 hours. After decomposition of excess reductant, the mixture was poured into 5% sulfuric acid–ice mixture. The product, bis-9-hydroxymethylanthracene, which separated at the interface, was isolated by filtration, 1.04 g., and treated with 100 ml. of hot pyridine. Petroleum ether was added to effect precipitation, yielding 600 mg. of finely divided white powder, m.p. 268–272°. The infrared spectrum was identical with the infrared spectrum of bis-9-hydroxymethylanthracene prepared by irradiation of 9-hydroxymethylanthracene: mixed m.p. 271–272°.

Bis-9-methyl anthroate was reduced by this procedure to give the same product, as determined by the identity of spectra and a mixed m.p. of 269–271°.

Reduction of the Photodimer of 9-Anthroic Anhydride.—The products of reduction are dependent on the concentration of the lithium aluminum hydride in ether. The addition of the cyclic anhydride to a solution of 2 g. of lithium aluminum hydride in 50 ml. of ether resulted in almost quantitative conversion to monomeric 9-hydroxymethylanthracene. A 10% yield of dimeric 9-hydroxymethylanthracene was obtained by the addition of 1.25 g. of the anhydride photomeride to a slurry of 3.5 g. of lithium aluminum hydride in 300 ml. of ether and subsequent stirring under reflux for 30 hours. The product, isolated by the above procedure, amounted to 90 mg. of a white powder, m.p. 270–271°. The infrared spectrum was identical with that of the photodimer of 9-hydroxymethylanthracene: mixed m.p. 270–271°.

Acid-catalyzed Dissociation of Bis-9-anthraldehyde.—To a clear saturated solution of bis-9-anthraldehyde in benzene was added a trace of *p*-toluenesulfonic acid. The initially colorless solution slowly turned yellow; heating a portion of the solution on the steam-bath resulted in the rapid development of the yellow color, attributed to the dissociation of the colorless dimer to the colored monomer.

CAMBRIDGE 39, MASSACHUSETTS

(28) A. Mustafa, *J. Chem. Soc.*, 1034 (1951), has reported a m.p. of 250° for a product formed by irradiation of 9-anthraldehyde in benzene.