1.0 mole), and 1 g. of hydroquinone were heated at 200° for 2 hr. The crude reaction mixture was fractionated through an 18-in. Vigreux column to yield 126 g. (82%) of a colorless oil, b.p. 85–86° (15 mm.); $n^{25}\text{D}$ 1.4606 [lit.[1] b.p. 88–90° (16 mm.), $n^{20}\text{D}$ 1.4655].

**Methyl 4-Methyl-3-cyclohexene-1-carboxylate (4-Isomer).**—The isoprene–methyl acrylate adduct (770 g., 5.00 moles) from combined 150°-reaction temperature runs was caused to react while stirring at 65° with 600 g. (15.0 moles) of sodium hydroxide dissolved in 3 l. of water. The mixture was clear after 2 hr. indicating that the reaction was complete. Concentrated sulfuric acid was added with stirring and cooling until the reaction mixture was acidic (pH 3). Benzene was added to dissolve the precipitated solid product. The organic and aqueous layers were separated and the aqueous solution was extracted with benzene. The combined benzene solutions were water-washed and the benzene was stripped under slightly reduced pressure. The crude product was purified by fractionation through a 6-in. Vigreux column to yield 677 g. (97%) of a mixture of 3-methyl- and 4-methyl-3-cyclohexene-1-carboxylic acid, a crystalline white solid, b.p. 162–164° (37 mm.), m.p. 51–74°.

This mixture of acids was recrystallized (four times) from petroleum ether (b.p. 60–100°) to a constant m.p. 98.5–99° (lit.[8] m.p. 99°). This procedure afforded 269 g. of pure 4-methyl-3-cyclohexene-1-carboxylic acid.

The esterification method of Lorette and Brown[9] was adopted for the preparation of pure methyl 4-methyl-3-cyclohexene-1-carboxylate. 4-Methyl-3-cyclohexene-1-carboxylic acid (140 g., 1.00 mole), methanol (160 g., 5.00 moles), 2,2-dimethoxypropane (208 g., 2.00 moles), and 2 ml. of concentrated hydrochloric acid were heated at the reflux temperature for 3 hr. Low boiling material was removed by distillation under reduced pressure. The residue was diluted with toluene and this solution was washed with water, 5% sodium bicarbonate solution, and once again with water. The toluene was removed by stripping under vacuum (water aspirator), and the crude product was fractionated through an 18-in. Vigreux column to afford 140 g. (91%) of methyl 4-methyl-3-cyclohexene-1-carboxylate, a colorless oil, b.p. 56–57° (2.2 mm.), $n^{25}\text{D}$ 1.4600. The capillary column gas chromatogram of the product indicated a single pure compound.

*Anal.* Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 70.12; H, 9.16.[10]

**Analytical Procedures.**—The gas chromatography analyses utilized a Perkin-Elmer Model 154 instrument equipped with 150 ft. of 0.01-in. i.d. stainless steel capillary "R" column coated with Ucon polyglycol LB-550-X, a highly sensitive hydrogen flame detector, and an "O" sample splitting device. Column temperature was not critical; reproducible results were obtained with a column temperature range of 100–175°. A temperature of ~125° was used in this work. Complete resolution of isomers was always achieved and control samples were liberally interspersed with the unknowns to ensure that constant equipment response was obtained.

Carbon disulfide solutions were prepared of the pure 4-isomer and a known mixture of the 3- and 4-isomers utilizing 100 mg. per 5 ml. of carbon disulfide. Infrared absorbance measurements were obtained at both 12.5 $\mu$ (4-isomer) and 12.7 $\mu$ (3-isomer) in a 1.0-mm. cell with a carbon disulfide blank as the reference for measurements for the standard solutions using a single beam spectrometer. Analytical and interference curves were plotted from the absorbance measurements obtained from the standard solutions. Samples were then prepared as 2% solutions in carbon disulfide, and measurements were made in the same manner. The concentrations of the 3- and 4-isomers were obtained by graphical solutions using the analytical and interference curves.

**Acknowledgment.**—The author is grateful to Dr. C. B. Roberts for the gas chromatography analyses and to R. T. Scheddel for devising the infrared spectroscopic method of analysis and for performing the measurements.

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[8] E. Lehmann and W. Paasche, *Ber.*, **68B**, 1068 (1935).

[9] N. B. Lorette and J. H. Brown, Jr., *J. Org. Chem.*, **24**, 261 (1959).

[10] Elemental analyses by the staff of Dr. P. H. Boyd of The Dow Chemical Company.

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# Diels–Alder Reactions of 9-Substituted Anthracenes. VI. 9-Anthryl Acetate, 9-Methoxyanthracene, and 9,10-Dimethoxyanthracene[1]

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9-Anthryl acetate gave only the vicinal type adduct with acrylic acid, and was less reactive in the Diels–Alder reaction than 9-methoxyanthracene. Acrylic acid, acrylonitrile, methyl acrylate, and acrylamide led to the vicinal adducts with 9-methoxyanthracene while allyl alcohol gave the nonvicinal adduct. The acrylic acid adducts of 9-anthryl acetate, 9-methoxyanthracene, and 9,10-dimethoxyanthracene upon treatment with hydrogen iodide underwent a ring opening to give 3-(10-keto-9,10-dihydro-9-anthryl)propionic acid, while the nonvicinal acid prepared by the oxidation of the allyl alcohol adduct gave only ether cleavage as did 9,10-dimethoxy-9,10-dihydro-9,10-ethanoanthracene. The maleic anhydride adducts of 9,10-dimethoxy-, 9,10-diacetoxy- and 9-methoxyanthracene led to (10-keto-9,10-dihydro-9-anthryl)succinic acid. Improved procedures for the preparation of 9-anthryl acetate, 9-methoxy- and 9,10-dimethoxyanthracene have been developed.

9-Anthraldehyde when condensed with monosubstituted dienophiles gave only vicinally substituted Diels–Alder adducts,[3] while 9-cyanoanthracene,[4] 9-anthraldehyde dimethyl acetal,[5] and 9-anthramide[6] gave in some cases both vicinal and nonvicinal adducts with the vicinal adduct, save in one case, predominating.

On the other hand 9-anthroic acid and acrylic acid as well as their salts gave only the nonvicinal adduct[7] and four of the six dienophiles, condensed with 9-nitroanthracene, gave predominantly the nonvicinal adduct.[6]

This indicates that as the substituent on the anthracene becomes more electron withdrawing the more likely it will be to give a nonvicinally substituted adduct. The one case which seems to be an exception for this is where sodium acrylate and sodium 9-anthroate gave the nonvicinal adduct, and this is presumably due to the repulsive effects of the carboxylate ionic moieties.

Since no 9-substituted anthracene bearing an *ortho-para* directing group has been studied in the Diels–

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[1] This work was supported by grants G-4178 and G-15157 from the National Science Foundation.

[2] National Science Foundation summer research participant.

[3] J. S. Meek, B. T. Poon, and S. J. Cristol, *J. Am. Chem. Soc.*, **74**, 761 (1952).

[4] J. S. Meek, J. R. Dann, and B. T. Poon, *ibid.*, **78**, 5413 (1956).

[5] J. S. Meek and J. R. Dann, *J. Org. Chem.*, **21**, 968 (1956).

[6] J. S. Meek, D. R. Wilgus, and J. R. Dann, *J. Am. Chem. Soc.*, **82** 2566 (1960).

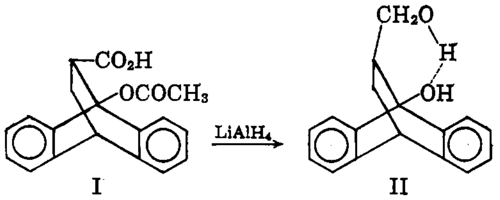
[7] K. Alder and K. Heimbach, *Chem. Ber.*, **86**, 1312 (1953).

Alder reaction with monosubstituted dienophiles, 9-anthryl acetate (9-acetoxyanthracene) and 9-methoxyanthracene were chosen for investigation.

9-Anthryl acetate was condensed with acrylic acid and gave a 50% yield of an acid. This adduct I was found to crystallize in two different forms, m.p. 220–226° and 184.1–184.7°. The latter is the more stable at room temperature since the higher melting crystals change to the lower melting form in a period of a few days. The infrared spectra of the two forms were superimposable.

In an effort to establish the structure of I, it was reduced with lithium aluminum hydride to the diol II. When the infrared spectrum of II in carbon tetrachloride was taken with a lithium fluoride prism two hydroxyl peaks were found at 2.768 and 2.867 $\mu$. The first peak is indicative of a free hydroxyl group while the second is at a wave length where hydrogen bonding is indicated,[8] and since the concentration of the diol was only $10^{-3}$ molar, this bonding was attributed to intramolecular hydrogen bonding.[9]

Therefore, the structure of 12-hydroxymethyl-9,10-dihydro-9,10-ethano-9-anthrol was assigned to compound II, since the nonvicinal adduct would have given a diol in which intramolecular hydrogen bonding would be impossible.

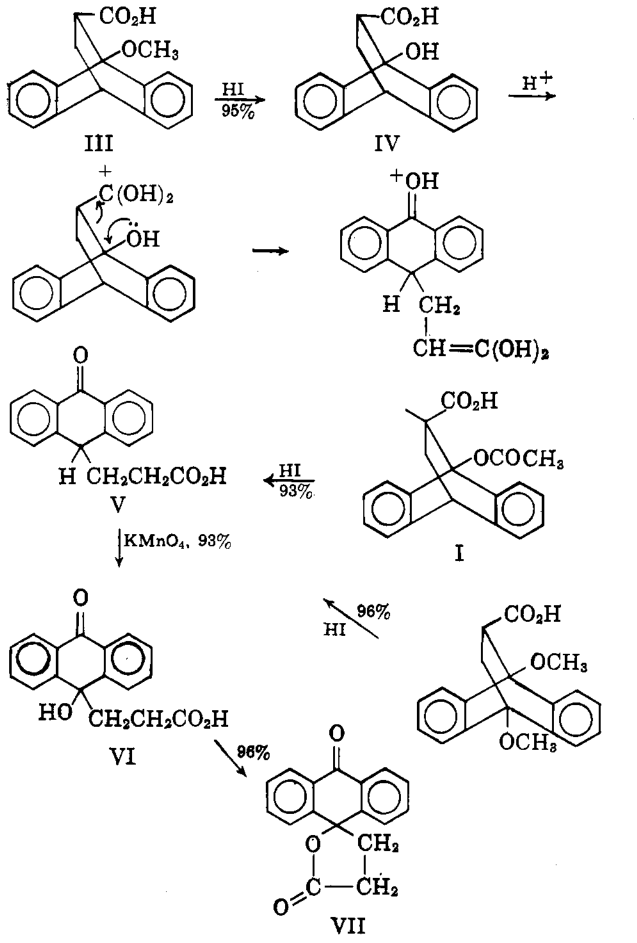


A high temperature was necessary for the condensation of 9-anthryl acetate and acrylic acid and the diene seemed less reactive than anthracene.

9-Methoxyanthracene has an electron-rich system which should make it a good diene and it was more reactive than 9-anthryl acetate since it condensed quickly on warming with acrylic acid and gave an an adduct with allyl alcohol.

When 9-methoxyanthracene was condensed with acrylic acid only adduct III was isolated. It was thought that if the adduct were the vicinal one, cleavage of the ether group would give IV since 9-methoxy-9,10-dihydro-9,10-ethanoanthracene has given the bridgehead alcohol.[10] Reduction with lithium aluminum hydride would then give II.

After refluxing III in a mixture of concentrated hydroiodic acid and acetic acid for thirty minutes a 95% yield of a product was obtained which turned yellow in alcohol but gave colorless crystals in benzene. The compound dissolved in aqueous alkali with the simultaneous appearance of a yellow color. The infrared spectrum of the white solid showed a carboxylic acid group with a peak at 5.9 $\mu$. A doublet at 6.05–6.28 $\mu$ indicated a carbonyl group between two aromatic rings.



The adduct was assigned a vicinal structure and the demethylated product the structure of V which arose apparently from a reverse type aldol condensation facilitated by the resonance energy gained in having a carbonyl group between two benzene rings. Compound V is a substituted anthrone and would be expected to turn yellow in alkali, as does anthrone, but not in alcohol.

This type of ring opening is new for bridgehead alcohols. Ordinarily a $\beta$-hydroxy acid having an $\alpha$ hydrogen atom would be expected to undergo dehydration but this reaction is prevented here since a double bond at the bridgehead carbon atom would have to be formed in violation of Bredt's rule.

If compound V was produced as indicated then it is obvious that compound I should give V on treatment with hydroiodic acid. This was tried and V was obtained in excellent yield.

In an effort to further the structure proof of V it was thought that oxidation would lead to anthraquinone. However, alkaline oxidation gave only a trace of anthraquinone and the main product was an acid which was colorless in basic solution. Its spectrum indicated a ketohydroxy acid and the compound was assigned structure VI. On melting, the compound appeared to lose water which indicated that either an olefinic bond or more likely a lactone had formed. Therefore, a sample was heated until water was no longer evolved. The product had an absorption of a five-membered lactone carbonyl group consistent with a spirolactone structure (VII).

The adduct of 9,10-dimethoxyanthracene and acrylic acid was prepared and gave a similar ring opening, but instead of yielding the hydroxy acid VI, reduction of the

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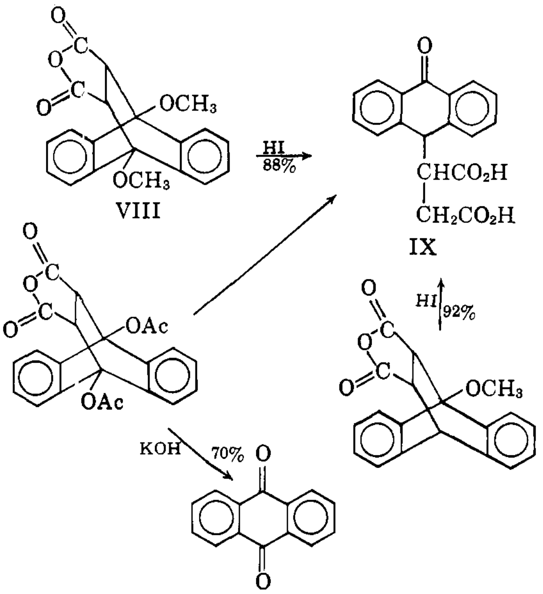
(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., Methuen and Co. Ltd., London, 1958, p. 96.

(9) A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

(10) W. B. Evans, Master's thesis, University of Colorado, 1953.

hydroxyl group occurred and V was obtained in 96% yield.

This same type of reduction occurred when the adduct VIII of 9,10-dimethoxyanthracene and maleic anhydride was treated with hydroiodic acid in acetic acid and (10-keto-9,10-dihydro-9-anthryl)succinic acid (IX) was formed. Cleavage of the maleic anhydride adduct of 9-methoxyanthracene also gave IX.

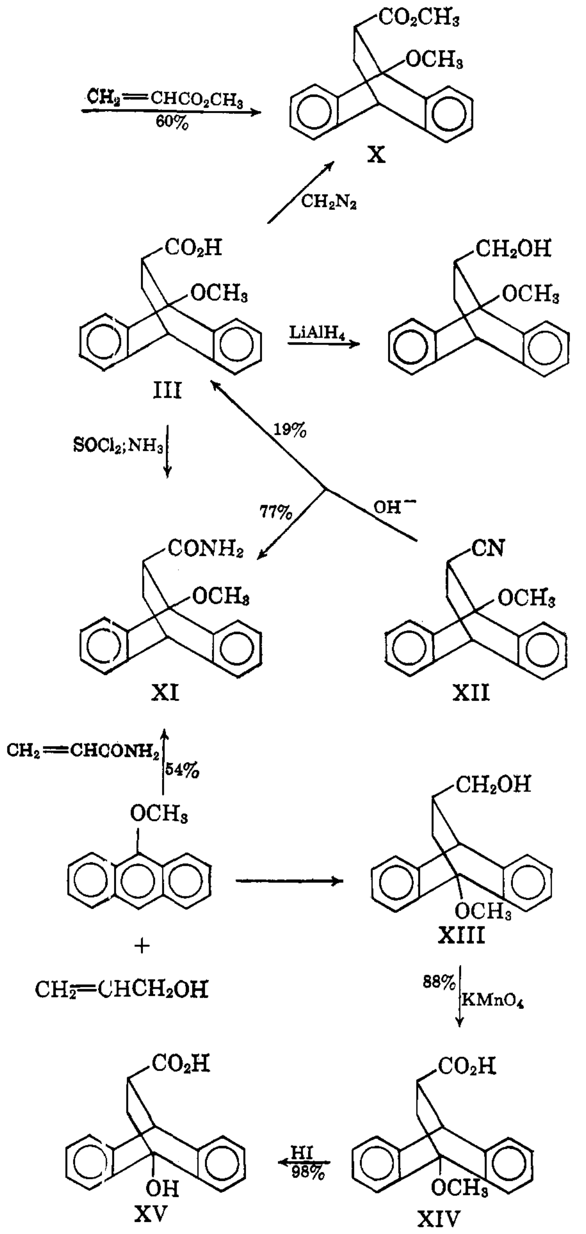


Presumably cleavage of VIII could occur at both bridge carbons and give anthraquinone. However, no trace of a neutral fraction could be found. Possibly the first cleavage is facilitated by the relief of ring strain and, therefore, the second cleavage lacking the extra driving force does not occur. However, it is more likely that once the bridge has been opened the second carbon atom is quickly reduced *via* a carbonium ion since it can now become a planar atom. This reaction pathway is excluded for bridgehead atoms and permits the slower cleavage reaction to be the only one possible.

The maleic anhydride adduct of 9,10-diacetoxyanthracene, when treated with hot alcoholic potassium hydroxide, gave a 70% yield of anthraquinone. Whether this is a reverse Diels–Alder reaction followed by air oxidation or whether it is a double ring opening going by a path similar to the acid-catalyzed reaction has not yet been determined. The anhydride could be converted into the diacid by heating in aqueous dioxane. The acid in turn gave IX in 92% yield.

A methyl acrylate adduct X of 9-methoxyanthracene was isolated and identified by its synthesis from the acrylic acid adduct III and diazomethane. The adduct XI of acrylamide was synthesized from III by treatment with thionyl chloride and ammonia. Acrylonitrile likewise gave the vicinal type adduct XII which upon treatment with base gave the amide XI and acid III.

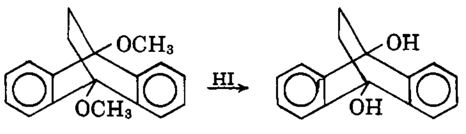
The vicinal structure assigned was checked by the n.m.r. spectrum of the nitrile which showed a triplet at 5.7 $\tau$ in chloroform indicative of a methylene group splitting the bridgehead hydrogen atom. 9,12-Dicyano-9,10-dihydro-9,10-ethanoanthracene[4] had a triplet at 5.45 $\tau$ while the 9,11-dicyano[4] isomer showed a doublet at 5.25 $\tau$ (acetonitrile with tetramethylsilane as standard).



The allyl alcohol-9-methoxyanthracene adduct was expected to be the same product as produced by the lithium aluminum hydride reduction of III, but the melting points and spectra indicated they were different, and for the first time in this series a nonvicinal adduct was obtained.

On oxidation it gave the isomer XIV of III that, in turn with hydroiodic acid in acetic acid, gave the hydroxy acid XV in which the bridge really was as stable as expected.

The ethylene adduct of 9,10-dimethoxyanthracene was prepared and upon cleavage gave a diol without a ring opening. This shows that a carboxyl group or perhaps some other negative group on the bridge is necessary for the ring opening.



The formation of a vicinal or nonvicinal adduct in each of the cases reported in this paper is in accordance with uniting the negative 10-position of the anthracene with the positive end of the dienophile. The resonance effects of the oxygen atom on the 9-position in the anthracenes permit an increase in electron density at the 10-position, as a positive $\beta$ atom of the acrylic derivative approaches. In allyl alcohol hyperconjugation would make the $\gamma$ atom negative and, therefore, lead to the nonvicinal adduct.

This reasoning was expressed previously[11] and does not provide an unfailing method for predicting positional isomerism in an adduct. Exceptions in the anthracene series have been found with 9-anthraldehyde,[3] 9-anthramide,[6] 9-cyanoanthracene,[4] and 9-nitroanthracene.[6]

In the course of preparing the starting anthracene derivatives, minor variations in technique have markedly improved results previously reported.

Liebermann and Topf heated anthrone and acetic anhydride to obtain 9-anthryl acetate[12] in unspecified yield. Barnett and Matthews reported that a better way to prepare the ester was to use pyridine as a sol vent for the reactants under carbon dioxide. They also failed to report a yield, but reported a melting point of 132–134°.[13] Fuson and Brasure also used pyridine as a solvent and after treatment of the product with Darco and numerous recrystallizations from ethanol obtained a 44% yield.[14]

This method has now been improved by using collidine as a solvent. One recrystallization of the product from ethanol without decolorization gave a good product in 81% yield.

Meyer and Schlösser[15] prepared 9-methoxyanthracene in a yield of 71% by treating a solution of anthrone alternately with alkali and methyl sulfate. Barnett, Cook and Matthews[16] reported this procedure was improved by using methyl *p*-toluenesulfonate and report a yield of 58% after the product was recrystallized from alcohol.

By adding the sodium hydroxide all at once and then methyl *p*-toluenesulfonate slowly and by recrystallizing the product from 2-propanol, we have increased the yield to 84%.

9,10-Dimethoxyanthracene has been prepared in about 43% yield by reducing anthraquinone with zinc and alkali, acidifying and isolating the product under carbon dioxide, and then methylating with methyl sulfate and alkali.[17] It has also been prepared in 60% yield by methylating the less available 10-methoxyanthrone.[18]

By immediate addition of methyl *p*-toluenesulfonate after an alkaline reduction the yield was raised to 92%.

## Experimental

**9-Anthryl Acetate.**—The previous method[13,15] was modified in the following manner. Anthrone, 12.3 g. (0.063 mole) was dissolved in a mixture of 82 ml. of collidine and 20 ml. of acetic anhydride. The resulting solution was heated on a steam bath under a nitrogen atmosphere for 2.5 hr. The contents of the reaction flask were cooled and poured into a mixture of 500 g. of ice and 90 ml. of concentrated hydrochloric acid. The mixture was stirred for 5 min. and the solid was collected by filtration. Recrystallization of the solid from 90% ethanol gave 12.05 g. (81%) of 9-anthryl acetate, m.p. 130–133°, lit.[14] m.p. 133–134°.

**9-Acetoxy-9,10-dihydro-9,10-ethanol -12 -anthracenecarboxylic acid** (I).—Freshly distilled acrylic acid, 6 g. (0.083 mole), was mixed with 2 g. (6.8 mmoles) of 9-anthryl acetate, 0.1 g. of hydroquinone, and 0.1 g. of 4-*t*-butylcatechol. The mixture was kept at 145–150° for 1 hr., then cooled, and poured into 30 ml. of carbon tetrachloride. The white precipitate which resulted was isolated by filtration. It weighed 1.68 g. (65% yield), m.p. 220–226°. Five recrystallizations from an acetone–petroleum ether (b.p. 85–100°) mixture produced a different crystalline modification with m.p. 184.1–184.7°. The infrared spectra of the two forms were superimposable.

*Anal.* Calcd. for $C_{19}H_{16}O_4$: C, 74.01; H, 5.23. Found: C, 73.86, H, 5.32.

**12-Hydroxymethyl-9,10-dihydro-9,10-ethano-9-anthrol** (II).—A solution of 1.3 g. (0.027 mole) of lithium aluminum hydride in 100 ml. of ether was added in a period of 1 hr. to a solution of 0.7 g. (0.00227 mole) of I in 20 ml. of tetrahydrofuran. Stirring was provided during the reaction and was continued for 1 hr. after the addition. Then the excess of lithium aluminum hydride was decomposed with ethyl acetate. After decomposing the complex with 6 ml. of water, the resulting precipitate was filtered and the solution was dried with magnesium sulfate. Evaporation of the organic solvent gave 0.45 g. (79%) of diol melting at 203–207°. Recrystallizations from aqueous ethanol increased the melting point to 209.2–209.9°.

*Anal.* Calcd. for $C_{17}H_{16}O_2$: C, 80.92; H, 6.39. Found: C, 81.10; H, 6.15.

The infrared spectrum of a $1 \times 10^{-3}\ M$ solution of this diol in carbon tetrachloride was taken by using a cell of 1-cm. thickness and a lithium fluoride prism. Absorption peaks appeared at 2.768 and 2.876 $\mu$ characteristic of free and intramolecularly bonded hydroxyl groups.

**Attempted Diels–Alder Reactions.**—Anthrone and vinyl acetate in pyridine or collidine in a sealed tube at 195° for 12 hr. gave decomposition.

9-Anthryl acetate with vinyl acetate in a sealed tube at 200° for 7 hr. also gave decomposition products as was also the case with vinylidene chloride in a sealed tube at 200° for 5 hr.

9-Anthryl acetate gave no reaction with allyl alcohol in a sealed tube at 180° for 18 hr.

**9-Methoxyanthracene.**—A modified method was used for this preparation. Ten grams (0.053 mole) of anthone was dissolved in 50 ml. of 2-propanol and 50 ml. of 20% sodium hydroxide was added and heated under a reflux condenser. To the boiling mixture was added methyl *p*-toluenesulfonate, a little at a time, until the color was practically discharged. An equal volume of water was added, and the mixture was cooled. The product was filtered, extracted with an alkaline sodium hydrosulfite solution until the extract was nearly colorless, and finally recrystallized from 2-propanol. The yield was 9.0 g. (81%), m.p. 95–96°, lit.[16] m.p. 97–98°.

**9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylic Acid** (III).—A mixture of 6.24 g. (0.03 mole) of 9-methoxyanthracene, 12 ml. of freshly distilled acrylic acid, and 0.10 g. of hydroquinone was heated to reflux. In 15–20 min. a white precipitate appeared. Heating was continued for another 30 min. The reaction mixture was allowed to cool and the precipitate filtered and washed with benzene to yield 6.70 g. (80%) of product melting at 207–209°. After two recrystallizations from benzene the product had a melting point of 209–210°.

*Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.78. Found: C, 77.09; H, 5.72.

**3-(10-Keto-9,10-dihydro-9-anthryl)propionic Acid** (V).—One gram of III (3.56 mmoles) was dissolved in 10 ml. of glacial acetic acid. Five grams of 47% hydroiodic acid (sp. gr. 1.5) was added and the solution was refluxed for 30 min. After cooling, the reaction mixture was added to 150–200 ml. of water. The resulting white precipitate was filtered and recrystallized from benzene to yield 0.90 g. (95%) of product melting between 159–170° dec. It was soluble in base or in excess alcohol and gave a yellow solution. The infrared spectrum indicated two carbonyl groups, with a peak at 5.9 $\mu$ and a doublet at 6.05–6.28 $\mu$.

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[11] J. S. Meek, J. W. Ragsdale, and S. J. Cristol, *J. Am. Chem. Soc.*, **70**, 2502 (1948).

[12] C. Liebermann and Topf, *Ber.*, **9**, 1201 (1876).

[13] E. deB. Barnett and M. A. Matthews, *J. Chem. Soc.*, **123**, 380 (1932).

[14] R. C. Fuson and D. E. Brasure, *J. Am. Chem. Soc.*, **77**, 3131 (1955).

[15] K. H. Meyer and H. Schlösser, *Ann.*, **420**, 126 (1921).

[16] E. deB. Barnett, J. W. Cook, and M. A. Matthews, *J. Chem. Soc.*, **123**, 1994 (1923).

[17] K. H. Meyer, *Ann.*, **379**, 37 (1911).

[18] C. Dufraisse and R. Priou, *Bull. soc. chim. France*, **6**, 1649 (1939).

Repeated recrystallizations from benzene gave white crystals with a decomposition point of 167–177°.

*Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30; neut. equiv., 268. Found: C, 76.46; H, 5.45; neut. equiv., 266.

In a similar fashion heating 0.50 g. of I for 2 hr. gave 0.40 g. (93%) of V as shown by its melting point of 161–179° dec., mixture melting point, and by comparison of the infrared spectra.

**3-(10-Keto-9-hydroxy-9,10-dihydro-9-anthryl)propionic Acid (VI).**—One gram (3.75 mmoles) of 3-(10-keto-9,10-dihydro-9-anthryl)propionic acid was dissolved in 50 ml. of approximately 0.15 *M* sodium hydroxide. Then 2.0 g. of solid potassium permanganate was added. The mixture was refluxed for 1.5 hr. After cooling, the excess permanganate was decomposed with sodium bisulfite and the solution was acidified with dilute sulfuric acid. The precipitate was removed by filtration. The 1.01 g. of product had a melting point of 165–170° with the evolution of water. The product was dissolved in sodium bicarbonate solution and filtered to yield 0.02 g. of anthraquinone, m.p. 283–284°. The filtrate was acidified and gave 0.98 g. (92.5%) of white crystals, m.p. 165–168°. Recrystallization from benzene raised the melting point to 167–168°.

*Anal.* Calcd. for $C_{17}H_{14}O_4$: C, 72.35; H, 4.99. Found: C, 72.36; H, 4.73.

**3-(10-Keto-9-hydroxy-9,10-dihydro-9-anthryl)propionic Acid Lactone (VII).**—A test tube containing 0.10 g. of 3-(10-keto-9-hydroxy-9,10-dihydro-9-anthryl)propionic acid (0.355 mmole) was placed in an oil bath at 170°. The tube was removed after complete melting and all signs of bubbling had ceased. The product was taken up in benzene–petroleum ether and 0.09 g. (96%) of material insoluble in sodium bicarbonate was obtained, m.p. 134.3–135°.

*Anal.* Calcd. for $C_{17}H_{12}O_3$: C, 77.27; H, 4.57. Found: C, 77.02; H, 4.77.

**9-Methoxy-9,10-dihydro-9,10-ethano-12-anthracenemethanol.**—One and a half grams (5.35 mmoles) of III was placed in an extraction thimble of a Soxhlet extractor. Half a gram (0.013 mole) of lithium aluminum hydride dissolved in 200 ml. of dry ether in a flask was attached to the extractor. The ether was refluxed for 48 hr. to extract the only slightly soluble acid, and the mixture was stirred for an additional 40 hr. The excess hydride was decomposed by slow addition of water and dilute hydrochloric acid added to release the product. The ether layer was separated from the aqueous solution and the aqueous solution extracted twice with additional ether. The combined ether extracts were dried over anhydrous sodium sulfate. Evaporation of the ether yielded 1.3 g. (92%) of a product, m.p. 82–84°. Recrystallization of the product from aqueous ethanol raised the melting point to 86–87°.

*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81. Found: C, 80.97; H, 7.08.

**Methyl 9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxylate (X).**—To 1.0 g. (3.57 mmoles) of III, covered with ether, was added an ethereal solution of diazomethane. As reaction occurred, the acid slowly dissolved. Diazomethane solution was continually added until the yellow color persisted and there was no further evidence of nitrogen evolution. The ether was evaporated by a stream of air to yield 1.05 g. (100%) of product, m.p. 131–134°. Recrystallization from methanol–water raised the melting point to 136.8–137.8°.

*Anal.* Calcd. for $C_{19}H_{18}O_3$: C, 77.90, H, 6.17. Found: C, 78.08; H, 6.39.

Three grams (0.014 mole) of 9-methoxyanthracene, 6 ml. of methyl acrylate (containing 0.10 g. of hydroquinone), and 10 ml. of xylene were placed in a metal bomb and heated for 14 hr. at a temperature of 130–145°. The xylene and excess methyl acrylate were evaporated under a stream of air. The resulting solid was taken up in hot methanol and allowed to crystallize, yield 2.5 g. (60%), m.p. 135–136°. A recrystallization raised the melting point to 136–137°. On admixture with the product obtained from III and diazomethane there was no depression in melting point. The infrared spectra of the two products were identical.

**9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxamide (XI).**—A solution of 2.08 g. (0.01 mole) of 9-methoxyanthracene, 2.0 g. (0.028 mole) of acrylamide, and 10 ml. of xylene was refluxed for 27 hr. The xylene was evaporated with a stream of air. The residue was taken up in hot methanol, and crystallization gave 2.1 g. of crude material having a melting point of 130–145°. The crude product was recrystallized from benzene to give 1.5 g. (54%) of product, m.p. 169–171°. Further recrystallization from benzene gave an analytical sample, m.p. 171–172°.

*Anal.* Calcd. for $C_{18}H_{17}NO_2$: C, 77.39; H, 6.13; Found: C, 77.31; H, 6.04.

Half a gram (1.78 mmoles) of the acid III was treated with 2 ml. of thionyl chloride on a steam bath for 15 min. The excess thionyl chloride was removed by distillation. The crude acid chloride was then added to 10 ml. of 20% ammonia solution. The precipitate was filtered and crystallized from benzene to yield 0.30 g. (60%) of product having a melting point of 168–170°. A mixture melting point determination with the product obtained from acrylamide and 9-methoxyanthracene showed no depression.

**9-Methoxy-12-cyano-9,10-dihydro-9,10-ethanoanthracene (XII).**—A mixture of 2.08 g. (0.01 mole) of 9-methoxyanthracene and 5 ml. of acrylonitrile was placed in a metal bomb and heated to a temperature of 160–170° for 4 hr. The product was added to benzene and evaporated with a stream of air to remove the excess acrylonitrile. The residue was taken up in hot methanol and allowed to crystallize, yield 2.1 g. (80.5%), m.p. 122–127°. Recrystallization from methanol raised the melting point to 130–131°.

*Anal.* Calcd. for $C_{18}H_{15}NO$: C, 82.73; H, 5.79. Found: C, 82.74; H, 5.61.

A mixture of 0.50 g. (1.91 mmoles) of the acrylonitrile adduct, 10 ml. of 1,2-propanediol, and 5 ml. of 20% sodium hydroxide was refluxed for 4 hr. The reaction solution was poured into a large volume of water to precipitate 0.41 g. (77%) of white material that melted at 169–170° after recrystallization from benzene. A mixture melting point with 9-methoxy-9,10-dihydro-9,10-ethanoanthracene-12-carboxamide showed no depression.

The filtrate from this precipitate was acidified with dilute hydrochloric acid to yield 0.10 g. (19%) of material melting at 209–210°. A mixture melting point with III showed no depression.

**9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid Anhydride.**—Two grams (0.0205 mole) of maleic anhydride and 4.16 g. (0.02 mole) of 9-methoxyanthracene were dissolved in 25 ml. of xylene. The solution was refluxed for 15 min. during which some of the adduct crystallized. The mixture was cooled and filtered to give 5.65 g. (92.5%) of product having a melting point 226–230°. After recrystallization from benzene the adduct melted at 230°.

*Anal.* Calcd. for $C_{19}H_{14}O_4$: C, 74.50; H, 4.61. Found: C, 74.54, H, 4.67.

**9,10-Dimethoxyanthracene.**—The procedure of Meyer[17] was modified and gave an improved yield. Anthraquinone, 10.4 g. (0.05 mole) was ground with 5.0 g. of zinc dust and placed in a reaction flask with 20 ml. of ethanol. One hundred milliliters of 20% sodium hydroxide was added and the total refluxed for 1 hr. until most of the anthraquinone was brought into solution. Methyl *p*-toluenesulfonate was then added, in small portions with continual stirring, until the color was discharged. The resulting precipitate was filtered, extracted with aqueous alkaline sodium hydrosulfite until the extract was practically colorless, and finally dissolved in excess benzene. Filtration and evaporation of the benzene yielded 11.0 g. of product melting at 198–199°, yield 92%. Recrystallization from benzene failed to raise the melting point.

**9,10-Dimethoxy-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid.**—Two grams (8.4 mmoles) of 9,10-dimethoxyanthracene and 0.10 g. of hydroquinone were placed in 5 ml. of boiling acrylic acid for 4.5 hr. After cooling, the mixture was poured into 10 ml. of acetic acid and 50 ml. of water. The resulting precipitate was filtered and dissolved in dilute sodium hydroxide and refiltered. This procedure yielded 0.10 g. of starting material. The filtrate was acidified with dilute hydrochloric acid to regenerate the adduct. Filtration gave 1.5 g. (60%) of the adduct. Recrystallization from either alcohol–water or benzene gave a product melting at 209.6–210.6°.

*Anal.* Calcd. for $C_{19}H_{18}O_4$: C, 73.53, H, 5.84. Found: C, 73.29, H, 5.76.

**Cleavage of 9,10-Dimethoxy-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid.**—When 0.55 g. (1.77 mmoles) of the acrylic acid adduct of 9,10-dimethoxyanthracene was refluxed for 1 hr. in 6 ml. of glacial acetic acid and 6 g. of hydroiodic acid, 0.45 g. (96%) of product was obtained. It was identified as V. Its melting point, mixture melting point, and spectrum were identical to that of the previously prepared acid. It also gave the same characteristic yellow color in basic solution or alcohol.

**9,10-Dimethoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic Acid Anhydride (VIII).**—A mixture of 4.76 g. (0.02 mole) of 9,10-dimethoxyanthracene and 2.00 g. (0.0205 mole) of maleic anhydride was placed in 20 ml. of xylene and heated to reflux for 1 hr. After cooling, the reaction mixture was filtered to yield 6.5 g. (96.5%) of product having a melting point of 248–250°. After recrystallization from benzene, the analytical sample melted at 248°.

*Anal.* Calcd. for $C_{20}H_{16}O_5$: C, 71.42; H, 4.79. Found: C, 71.24; H, 4.78.

**(10-Keto-9,10-dihydro-9-anthryl)succinic Acid (IX).**—Three grams (8.94 mmoles) of VIII was mixed with 50 ml. of acetic acid and 25 ml. of hydroiodic acid and refluxed for 6 hr. It took 3 hr. for solution to occur. Concentration of the solution to 15 ml. and filtration gave 2.3 g. of white solid, m.p. 192–194° (83%). Recrystallization from aqueous alcohol gave a melting point of 194.3–195.3° with bubbling presumably due to the formation of the anhydride. The carbonyl region of the spectrum was similar to V.

*Anal.* Calcd. for $C_{18}H_{14}O_5$: C, 69.67; H, 4.54. Found: C, 69.61; H, 4.65.

The adduct of 9-methoxyanthracene and maleic anhydride was similarly cleaved to IX in 92% yield; m.p. 194–195°.

Three grams of 9,10-diacetoxyanthracene[19] (0.01 mole) was heated with 25 g. (0.25 mole) of maleic anhydride at 160° under an atmosphere of nitrogen for 5.5 hr. Water was used to remove the excess maleic anhydride, and 3.74 g. (95%) of the adduct was obtained melting at 240–243°. Five recrystallizations from chloroform gave an analytical sample, m.p. 246.9–248.7° dec.

*Anal.* Calcd. for $C_{22}H_{16}O_7$: C, 67.34; H, 4.11. Found: C, 67.47; H, 4.31.

When the adduct was heated with 5% ethanolic potassium hydroxide a 70% yield of anthraquinone was obtained. When the adduct was heated under reflux conditions for 36 hr. with a 75% aqueous dioxane solution, a 58% yield of the diacid was obtained as indicated by an infrared spectrum. The melting point was the same as that of the anhydride presumably due to anhydride formation on heating.

When 1 g. of 9,10-diacetoxy-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid was heated with hydroiodic acid in acetic acid, 0.72 g. of IX was obtained (92%).

**9-Methoxy-9,10-dihydro-9,10-ethanoanthracene-11-methanol (XIII).**—Twenty milliliters of allyl alcohol, 2.08 g. (0.01 mole) of 9-methoxyanthracene, and a trace of hydroquinone were placed in a metal bomb and heated at 185–190° for 14 hr. after 5 hr. of heating to reach this temperature. With periodic addition of benzene, the reaction mixture was evaporated with a stream of air to remove excess allyl alcohol. The resulting oil was taken up in ethyl ether and filtered to remove insoluble tar. After evaporation of the ether, the oil was partially crystallized by the addition of a low boiling petroleum ether–benzene mixture. Filtration yielded a crude product melting at 130–136°. Recrystallization from aqueous methanol resulted in the lowering of the melting point. After four recrystallizations, 0.50 g. of product (18.7%) had a melting point of 121.8–123.3° in contrast to m.p. 86–87° found for the 12-methanol. The infrared spectrum was different from that obtained for the isomer produced by the reduction of the 12-carboxylic acid.

*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.18; H, 6.81. Found: C, 81.21; H, 6.68.

Evaporation of the petroleum ether–benzene filtrate yielded an oil which solidified to a hard resinous mass. This did not yield any identifiable substance.

**9-Methoxy-9,10-dihydro-9,12-ethanoanthracene-11-carboxylic acid (XIV).**—A solution of 0.15 g. (0.565 mmole) of XIII in 4 ml. of acetic acid and 2 ml. of water evolved heat when 0.30 g. of solid potassium permanganate was added. The reaction mixture was heated to a gentle boil for 5 min. and then 10–12 ml. of water was added. The excess permanganate was decomposed with sodium bisulfite. The solution remained acidic and when cooled, the resulting precipitate was filtered; yield, 0.14 g. (87.5%), of a white product, m.p. 180–185°. After recrystallization from a small amount of benzene the melting point was 189–191°. This acid was very soluble in benzene and alcohol whereas the isomeric 12-carboxylic acid was only slightly soluble in these solvents. Their infrared spectra were different, especially in the fingerprint region.

*Anal.* Calcd. for $C_{18}H_{16}O_3$: C, 77.12; H, 5.78. Found: C, 77.02; H, 5.72.

**9-Hydroxy-9,10-dihydro-9,10-ethanoanthracene-11-carboxylic Acid (XV).**—Treatment of 0.3 g. of XIV in refluxing acetic acid–hydroiodic acid for 1 hr. gave 0.28 g. (98%) of product melting at 194–196°. The infrared showed no carbonyl doublet between 6.05 and 6.28 $\mu$ but showed an additional hydroxyl peak at 2.96 $\mu$. The analytical sample melted 196–197° after crystallization from aqueous ethanol.

*Anal.* Calcd. for $C_{17}H_{14}O_3$: C, 76.67; H, 5.30. Found: C, 76.49; H, 5.49.

**9,10-Dimethoxy-9,10-dihydro-9,10-ethanoanthracene.**—Ethylene was heated under pressure with 8 g. of dimethoxyanthracene in benzene at 175° for 24 hr. After removal of the benzene and crystallization from alcohol 3.9 g. of product melting at 132–135° was obtained. The analytical sample melted at 135–136°.

*Anal.* Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.03; H, 6.79.

Cleavage of 1.6 g. of the dimethyl ether gave 1.3 g. (90%) of 9,10-dihydro-9,10-ethano-9,10-anthradiol, m.p. 267–268°. This was identical with the diol obtained in 78% yield by the lithium aluminum hydride reduction of the ethylene adduct of 9,10-diacetoxyanthracene.[20]

**Spectra.**—Infrared spectra were determined with Perkin-Elmer Model 21 and Beckmann-IR5 spectrophotometers. Spectra of the compounds in this paper are available from S. P. Sadtler and Son, Inc., Philadelphia 3, Pennsylvania.

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[19] E. deB. Barnett, N. F. Goodway, A. G. Higgens, and C. A. Lawrence, *J. Chem. Soc.*, 1224 (1934).

[20] The reduction was carried out by T. Tiedeman in this laboratory and his diol was identical with the product obtained by treating 9,10-diamino-9,10-dihydro-9,10-ethanoanthracene with nitrous acid [T. W. Campbell, V. E. McCoy, J. C. Kauer, and V. S. Foldi, *J. Org. Chem.*, **26**, 1422 (1961)].