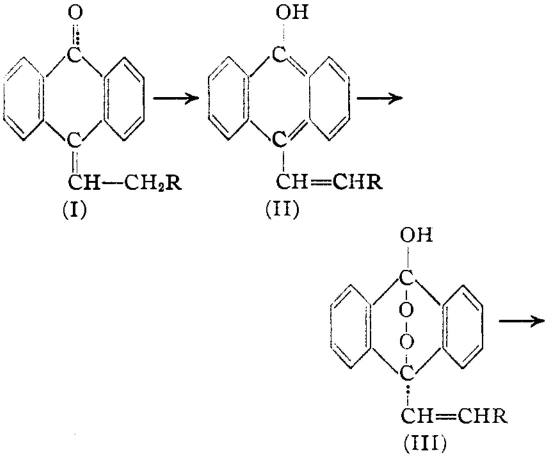
[Contribution from the Research Laboratories of The Glidden Company, Soya Products Division]

Conjugated Systems. V. A 1,7-Shift of Hydrogen in the Conversion of Alkylidene Anthrones into Vinyl Anthranols[1]

By Percy L. Julian, Wayne Cole and Edwin W. Meyer

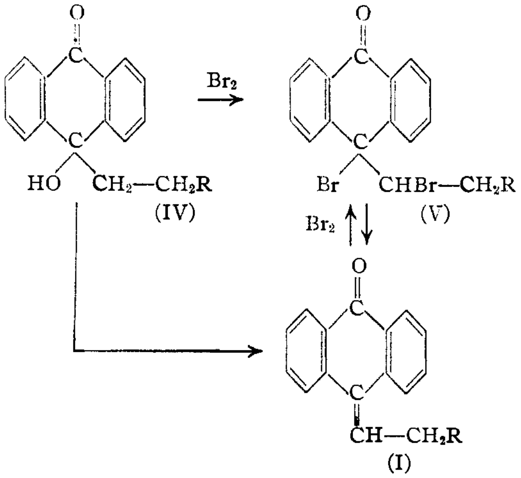
Several years ago we reported[2] that our attempts to prepare ethylideneanthrone (I, R = H) in the presence of oxygen led to anthraquinone and acetaldehyde. In view of the stability of methyleneanthrone and benzalanthrone it seemed inconceivable that in ethylideneanthrone the double bond at the 10-position of the anthracene nucleus was the focal point of oxidation, and we therefore suggested that ethylideneanthrone existed in equilibrium with an enol modification, vinylanthranol (II, R = H). This tautomeric modification would be expected then to undergo 1,4-addition of oxygen to the reactive 9- and 10-positions to form the peroxide (III, R = H), which in turn would decompose into anthraquinone and vinyl alcohol in a manner analogous to the decomposition of alkylanthranol peroxides.[3]



[RCH=CHOH] + Anthraquinone

The tautomerism suggested to explain the behavior of ethylideneanthrone involves a 1,7-shift of hydrogen, and to our knowledge no case of such a shift of hydrogen from carbon to oxygen had previously been reported. It therefore appeared desirable to obtain more conclusive proof for such a tautomerism by isolating the intermediate vinylanthranols (II) or derivatives of them, and also to determine whether this behavior is generally characteristic of alkylideneanthrones. This paper reports the successful realization of these aims.

We have employed several methods for preparing the alkylideneanthrones (I). The one found most generally useful involves elimination of the elements of water from alkylhydroxyanthrones (IV), using either concentrated sulfuric acid[4] or a mixture of sulfuric acid and acetic acid under nitrogen. In this manner ethylideneanthrone and *n*-propylideneanthrone were obtained as oils, while the *n*-butylidene- and isoamylideneanthrones were obtained as crystalline solids. The method was not applicable to the preparation of isopropylideneanthrone from the corresponding isopropyl-hydroxy-anthrone, and the mechanism of dehydration in this case is still under investigation.



When titrated with bromine in chloroform solution, ethylideneanthrone and butylideneanthrone yielded crystalline dibromides (V). These dibromides have been prepared also by the action of bromine on the alkyl-hydroxy-anthrones (IV) in acetic acid solution. Removal of the bromine from the butylideneanthrone dibromide with chromous chloride[5] thus offered an alternative, but less satisfactory, method for preparing butylideneanthrone.

Each of these alkylideneanthrones undergoes atmospheric oxidation and slowly yields anthraquinone and an aldehyde. Similar results were obtained when the elimination of the elements of water from the alkyl-hydroxy-anthrones (IV) was carried out in the presence of oxygen. Thus ethylideneanthrone gave acetaldehyde and anthraquinone; propylideneanthrone yielded propionaldehyde and anthraquinone; butylideneanthrone and isoamylideneanthrone gave butyraldehyde and isovalerylaldehyde, respectively. It therefore appears plausible that each of these anthrones is capable of existing in an anthranol

---

(1) Presented in part as paper No. IV in this series at the Fall meeting of the American Chemical Society, Boston, 1939.

(2) Julian, Cole and Wood, This Journal, **57**, 2509 (1935).

(3) (a) Julian and Magnani, *ibid.*, **56**, 2174 (1934); (b) Julian and Cole, *ibid.*, **57**, 1607 (1935); (c) Julian, Cole and Diemer, *ibid.*, **67**, 1721 (1945).

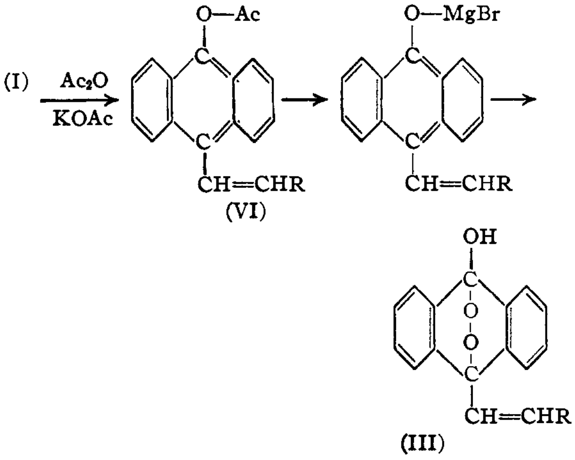
(4) *Cf.* Liebermann, *Ann.*, **212**, 96 (1882).

(5) *Cf.* Julian, Cole, Magnani and Meyer, This Journal, **67**, 1728 (1945).

modification, which latter undergoes oxidation with atmospheric oxygen to form peroxides similar to those already reported for alkyl anthranols. These peroxides in their turn suffer 1,4-elimination of the elements of vinyl alcohols, and such a transannular elimination of the elements of alcohols is exactly parallel to the behavior of alkylanthranol peroxides on heating.[2,3]

Methyleneanthrone and benzalanthrone are stable at atmospheric conditions and do not belong to the above-mentioned class. It is clear that only those alkylideneanthrones possessing the necessary hydrogen atom for enolization by 1,7-shift of hydrogen exhibit peroxide formation by 1,4-addition of oxygen to the meso positions of the anthranol ring.

Proof that such enolization occurs was obtained by preparing an enol acetate (VI) from each of the alkylideneanthrones by the action of acetic anhydride in the presence of anhydrous potassium acetate. These anthranyl acetates were yellow solids which exhibited strong blue fluorescence in dilute solutions. The nature of the alkenyl group in the 10-position was established by ozonization. Thus vinylanthranyl acetate (VI, R = H) afforded formaldehyde, and isopentenylanthranyl acetate (VI, R = i-C_3H_7) gave isobutyraldehyde, identified as the 2,4-dinitrophenylhydrazones. The anthranyl acetates, in contrast to the free anthranols, appeared to be stable in the presence of oxygen.



(VI)

(III)

The desired peroxides (III) were obtained by treating the anthranyl acetates (VI) with methylmagnesium bromide, followed by hydrolysis and treatment with oxygen. The propenylanthranol peroxide (III, R = CH_3) was crystallized and analyzed, but in the other cases the peroxides were not purified. They behaved as typical anthranol peroxides, decomposing on heating with the formation of anthraquinone and the elements of alcohols.

These findings are in significant agreement with the principle of vinylogy[6] in that the influence of a carbonyl group upon the mobility of a hydrogen atom is transmitted through a conjugated system of two unsaturated linkages.

Experimental[7]

10-Vinylanthranyl Acetate (VI, R = H).—Ethylideneanthrone was prepared by thermal dehydration of 10-ethyl-10-hydroxyanthrone in the known manner,[2,8] and by the acetic acid–sulfuric acid dehydration procedure which is described below for the preparation of butylideneanthrone. In each instance it was an ether-soluble red sirup which showed no promise of crystallization, and which slowly underwent air oxidation to anthraquinone. It has been characterized by addition of one mole of bromine in chloroform solution to form the known 10-bromo-10-α-bromoethylanthrone, m. p. 121–123°,[8] and by its enol acetate.

A mixture of 9 g. of the sirupy ethylideneanthrone, 16 g. of anhydrous potassium acetate and 250 ml. of acetic anhydride was refluxed for eight hours, during which it developed a bright blue fluorescence. A major portion of the acetic anhydride was distilled, then the remainder was hydrolyzed with water. The product was dissolved in ether, washed, concentrated and crystallized from methanol, giving 6.2 g. of vinylanthranyl acetate as brown-yellow plates, m. p. 139–142°. Recrystallization from acetone–methanol gave yellow crystals, m. p. 143–145°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 81.88; H, 5.55.

A solution of 2.2 g. of the vinylanthranyl acetate in 80 ml. of glacial acetic acid was cooled to 15° and treated with 5% ozone for eight minutes at a rate of 1 liter per min. Water and zinc dust were added, and the mixture was slowly distilled. The first 40 ml. of distillate contained formaldehyde which was converted into 0.3 g. of the 2,4-dinitrophenylhydrazone, m. p. 164–165°.

When 1 g. of the vinylanthranyl acetate in 40 ml. of ethyl acetate was shaken with hydrogen and 0.1 g. of platinum oxide, approximately one mole-equivalent of hydrogen was absorbed during thirty minutes. The product yielded 0.2 g. of **10-ethylanthranyl acetate,** m. p. 136–138°, together with some recovered vinylanthranyl acetate and a wax with a terpene odor.

For comparison, a sample of 10-ethylanthranyl acetate was prepared by addition of methylmagnesium bromide to methyleneanthrone and treating the ethylanthranoxymagnesium bromide so formed[8b] with acetyl chloride. The crude product, m. p. 130–134°, which separated in 85% yield from ether–petroleum ether, was recrystallized from acetone, which gave straw-yellow flakes, m. p. 136–138°. Dilute solutions of the acetate displayed strong blue fluorescence.

Anal. Calcd. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.54; H, 6.18.

10-Vinylanthranol Peroxide (III, R = H).—Two grams of vinylanthranyl acetate was dissolved in 140 ml. of absolute ether and added to a Grignard solution containing 0.1 mole of methylmagnesium bromide. After refluxing gently for six hours, the mixture was treated with ice and ammonium chloride; then oxygen was bubbled through the washed ether solution for two hours. Addition of petroleum ether to the concentrate gave the crude peroxide as a tan gum which slowly formed a few crystals (m. p. 112–117°, dec.), but no pure sample could be obtained.

A sample of this crude peroxide was decomposed by heating to 250° for ten minutes. The volatile products were trapped in ethanol, and the acetaldehyde was identified by conversion into the 2,4-dinitrophenylhydrazone. The residue from the decomposition yielded anthraquinone as the only ether-insoluble product, but a considerable amount of tar was formed during the decomposition.

---

(6) Fuson, *Chem. Rev.*, **16**, 1 (1935).

(7) The carbon–hydrogen analyses were run by Mr. R. A. Herness of this Laboratory.

(8) Liebermann, *Ber.*, **13**, 1598 (1880).

10-Propenylanthranyl Acetate (VI, R = CH_3).—10-Propyl-10-hydroxyanthrone[9] (m. p. 169–171°) was prepared by the addition of *n*-propylmagnesium bromide to a stirred suspension of anthraquinone in benzene. Five grams of the powdered propyl-hydroxy-anthrone was dissolved portionwise in 25 ml. of cold concd. sulfuric acid, and then allowed to stand under nitrogen at room temperature for one and one-half hours. It was then poured over crushed ice and extracted with ether. The ether solution was washed, dried and concentrated *in vacuo*. The propylideneanthrone so prepared was a red oil containing a minute quantity of suspended solid (anthraquinone). Attempts to crystallize the material were unsuccessful.

The crude propylideneanthrone was dissolved in 80 ml. of acetic anhydride containing 7 g. of fused potassium acetate, and the solution was refluxed for eight hours. The product was diluted with water, extracted with ether, washed with dilute alkali and water, concentrated and then crystallized from aqueous methanol. The propenylanthranyl acetate, 4.9 g., m. p. 180–190°, was recrystallized from benzene–petroleum ether, which raised the melting point to 194–197°.

Anal. Calcd. for $C_{19}H_{16}O_2$: C, 82.55; H, 5.83. Found: C, 82.89; H, 6.31.

10-Propenylanthranol Peroxide (III, R = CH_3).—A solution of 2.3 g. of propenylanthranyl acetate in 50 ml. of dry benzene was added dropwise to an ethereal solution of 0.05 mole of methylmagnesium bromide, and the mixture was refluxed for two hours. The magnesium compound was hydrolyzed with ice and ammonium chloride, and the washed ethereal solution (green fluorescence) was treated with oxygen for two hours, during which the fluorescence disappeared. The solution was concentrated *in vacuo* and petroleum ether added. The tan solid which separated melted at 139–141°, with dec., and weighed 1.9 g. Recrystallization from benzene–petroleum ether did not change the decomposition point.

Anal. Calcd. for $C_{17}H_{14}O_3$: C, 76.68; H, 5.29. Found: C, 76.86; H, 5.60.

Decomposition of Propenylanthranol Peroxide.—A one-half-gram sample of the peroxide was decomposed by heating in a distilling flask. After cooling slightly, a few ml. of glacial acetic acid was added and distilled. Treating the distillate with 2,4-dinitrophenylhydrazine gave an orange hydrazone, m. p. 148–152°, which gave no depression in melting point when mixed with an authentic sample of propionaldehyde 2,4-dinitrophenylhydrazone. The residue from the distillation contained anthraquinone together with unidentified products.

10-*n*-Butyl-10-hydroxyanthrone (IV, R = C_2H_5).—A suspension of 150 g. of anthraquinone in 500 ml. of benzene was stirred at room temperature while a solution of 0.5 mole of *n*-butylmagnesium bromide in 300 ml. of ether was added dropwise during two and one-half hours. The reaction mixture was poured into ice and dilute hydrochloric acid, then filtered first through glass wool then through paper to remove the excess anthraquinone. The washed ether–benzene solution yielded 66 g. of the "butyloxanthrone," which crystallized from ether (or from acetic acid) as colorless prisms, m. p. 121–122°.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 80.81; H, 6.97.

Boiling glacial acetic did not change the butyloxanthrone, but acetic anhydride yielded **10-*n*-butyl-10-acetoxyanthrone**, colorless prisms, m. p. 126°.

Anal. Calcd. for $C_{20}H_{20}O_3$: C, 77.89; H, 6.54. Found: C, 78.29; H, 6.77.

10-Butylideneanthrone (I, R = C_2H_5).—A solution of 9 g. of the butylhydroxy-anthrone in 100 ml. of glacial acetic acid was treated with 1 ml. of concd. sulfuric acid and held in a nitrogen-filled flask for twenty-four hours at 50° then for twenty-four hours at room temperature. Ten ml. of water was added, and the anthraquinone which separated was removed by filtration. The liquor was diluted with 100 ml. of water and cooled, whereby the crude butylideneanthrone separated as an oil which slowly crystallized. Recrystallization from methanol gave 4 g. of yellow needles, m. p. 48–50°.

Anal. Calcd. for $C_{18}H_{16}O$: C, 87.06; H, 6.45. Found: C, 86.65; H, 6.73.

After standing for one week in a vial at room conditions, the butylideneanthrone became a yellow wax having the rancid odor of butyraldehyde. An ether solution of the wax deposited yellow needles of anthraquinone, m. p. 278–281°.

10-α-Bromobutyl-10-bromoanthrone (V, R = C_2H_5).—A solution of 0.2 g. of the butylideneanthrone in 15 ml. of glacial acetic acid rapidly decolorized one mole-equivalent of bromine. The solution was diluted with water and scratched, whereupon 0.2 g. of white plates of the dibromide, m. p. 135–136°, separated. The same dibromide was prepared directly from the butyloxanthrone. A solution of 2.66 g. (0.01 mole) of butyl-hydroxy-anthrone in 40 ml. of glacial acetic acid was treated with 1.7 g. of bromine and 1 drop of hydrobromic acid at 90° for twenty minutes. The nearly colorless solution was diluted with 5 ml. of water and cooled, whereupon 3.3 g. of white plates of the dibromide, m. p. 133–135°, separated. A sample which was recrystallized from acetone–methanol melted at 135–136°.

Anal. Calcd. for $C_{18}H_{16}OBr_2$: Br, 39.2. Found: Br, 39.6.

Debromination with either chromous chloride in aqueous acetic acid[5] or with sodium iodide in acetone gave the butylideneanthrone, m. p. 46–48°, but this could be crystallized only with difficulty.

10-Butenylanthranyl Acetate (VI, R = C_2H_5).—Eight grams of butylideneanthrone, 12 g. of potassium acetate and 250 ml. of acetic anhydride were refluxed gently for thirty-six hours, then most of the acetic anhydride was distilled *in vacuo*. The residue was treated with methanol and water, and extracted with ether. From the washed, blue-fluorescent ether solution there was obtained 5.1 g. of the enol acetate, m. p. 113–115°. It recrystallized from acetone as yellow flakes, m. p. 115–116°.

Anal. Calcd. for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.27; H, 6.48.

Concentrated solutions of the acetate were yellow and non-fluorescent, but dilute ether or acetone solutions displayed a strong blue fluorescence. Passing oxygen through the solutions did not alter the properties of the acetate.

10-Butenylanthranol Peroxide (III, R = C_2H_5).—A solution of 3 g. of the butenylanthranyl acetate in 100 ml. of absolute ether was added to a Grignard solution containing 0.1 mole of methylmagnesium bromide in 200 ml. of ether. A yellow precipitate formed promptly. The mixture was stirred and refluxed for five hours, then worked up in the usual manner, using ammonium chloride to dissolve the magnesium salts. Oxygen was bubbled through the ether solution of butenylanthranol for one hour. Evaporation of the remaining solvent left a yellow wax, which could not be crystallized.

In order to obtain the pyrolysis products from the peroxide, the wax was placed in a small flask under reflux, four drops of *n*-propanol was added (to form a blanket of vapor over the material) then the flask was heated to 180° for thirty minutes. About 15 ml. of propanol was added, then 10 ml. was distilled. The distillate yielded butyraldehyde, which was identified by odor and by conversion into 0.2 g. of butyraldehyde 2,4-dinitrophenylhydrazone, m. p. 119–121°. The residue from the pyrolysis yielded (by sublimation) yellow needles of anthraquinone, m. p. 270–275°.

10-Isoamyl-10-hydroxyanthrone was prepared according to the method of Liebermann[10] as described by Ghigi.[11] Thirty grams of anthraquinone and 25 g. of isoamyl bromide gave 22 g. of the crude isoamylhydroxyanthrone melt-

---

[9] Hallgarten, *Ber.*, **22**, 1071 (1889).

[10] Liebermann, *Ann.*, **212**, 96 (1882).

[11] Ghigi, *Ber.*, **70**, 2469 (1937).

ing at 112–116°. It was purified by recrystallization from benzene–petroleum ether.

10-Isoamyl-10-acetoxyanthrone.—A solution of 5 g. of isoamylhydroxyanthrone in 20 ml. of acetic acid and 5 ml. of acetic anhydride was refluxed for two hours. The chilled solution was diluted with a small quantity of water and the crystalline material was separated. The crystals weighed 3.4 g. and melted at 105–108.5°. Several recrystallizations from methanol gave long, colorless prisms melting at 107.5–109°.

Anal. Calcd. for $C_{21}H_{22}O_3$: C, 78.22; H, 6.88. Found: C, 77.88; H, 7.08.

Decomposition of Isoamylhydroxyanthrone.—A solution of 2.5 g. of isoamylhydroxyanthrone in 25 ml. of acetic acid containing 10 drops of concd. sulfuric acid was allowed to stand in a stoppered flask for nine days. A crystalline solid slowly separated during this period. The yellow crystalline solid, 0.2 g. of anthraquinone, was separated and the remaining solution was distilled. About 15 ml. of distillate was collected and treated with an ethanolic solution of 2,4-dinitrophenylhydrazine. The orange hydrazone, 0.1 g., melted at 123–126° and gave no depression in melting point when mixed with a sample of isovaleraldehyde 2,4-dinitrophenylhydrazone. The residue of distillation deposited another 0.2 g. of anthraquinone.

Isoamylideneanthrone (I, R = i-C_3H_7).—The anthrone was prepared by an adaptation of the procedure described by Liebermann.[10] Ten grams of isoamylhydroxyanthrone was dissolved portion-wise in 50 ml. of concd. sulfuric acid chilled in an ice-bath. The deep red solution was allowed to stand in a stoppered flask at room temperature for two hours. The solution was then poured over crushed ice and extracted with ether. The ether solution was washed, and a cuff of insoluble anthraquinone was separated. The residue after removal of ether from the dried solution was crystallized from methanol, which deposited 6.3 g. of pale yellow needles melting at 68-72°. Recrystallization from methanol raised the melting point to 72.5–74°. The isoamylideneanthrone is quite soluble in ether and petroleum ether and moderately soluble in ethanol and methanol. Upon exposure to air, decomposition takes place, and recrystallization of material after such exposure yields considerable anthraquinone. The compound is reasonably stable when kept *in vacuo*.

When examined in the Grignard machine, 0.80 millimole of the isoamylideneanthrone gave 0.15 millimole of gas and 0.62 millimole of addition.

10-Isopentenylanthranyl Acetate (VI, R = i-C_3H_7).—A solution of 4 g. of isoamylideneanthrone in 100 ml. of acetic anhydride containing 8 g. of freshly-fused potassium acetate was refluxed for eight hours. The solution gradually darkened and took on a blue fluorescence. It was then diluted with water and the product separated by ether extraction. Crystallization of the ether soluble material from methanol gave 4.0 g. of crude tan solid melting at 98–104°. Several recrystallizations from methanol gave yellow needles melting at 105–107°.

Anal. Calcd. for $C_{21}H_{20}O_2$: C, 82.85; H, 6.64. Found: C, 82.57; H, 6.68.

Ozonolysis of Isopentenylanthranyl Acetate.—A stream of ozone (5% by volume) was passed through a solution of 1.5 g. of isopentenylanthranyl acetate in 75 ml. of acetic acid at the rate of 0.5 liter/min. for ten minutes. The blue fluorescence gradually disappeared, and toward the end of the period a small quantity of solid separated. Five grams of zinc dust was added to the solution, and about 30 ml. was distilled through a short Vigreaux column. The distillate contained isobutyraldehyde, which was identified by conversion into 0.35 g. of the 2,4-dinitrophenylhydrazone melting at 180–182°. Recrystallization from methanol gave orange needles which melted at 182–183° and gave no depression in melting point when mixed with a known sample of isobutyraldehyde 2,4-dinitrophenylhydrazone.

The non-volatile portion was separated into acidic and neutral fractions. The acidic material proved to be a small quantity of dark gum. From the neutral fraction, a small quantity of anthraquinone was isolated; however, the remainder could not be crystallized.

10-Isopentenylanthranol Peroxide and its Decomposition.—An ethereal solution of 2.5 g. of the enol acetate was added to a solution containing 0.05 mole of methylmagnesium bromide. The murky, yellow solution was stirred for one hour and then refluxed for two hours. The mixture was decomposed with ice and ammonium chloride and extracted with ether. Oxygen was bubbled through the washed ether solution for two hours, during which the initial green fluorescence disappeared. The ether was removed *in vacuo*, leaving the crude isopentenylanthranol peroxide as a brown gum weighing 2.4 g.

A sample of the peroxide was heated in a distilling apparatus to about 130°, at which point it decomposed suddenly. A few ml. of glacial acetic acid was added and distilled. From the volatile product only isobutyraldehyde could be identified by conversion into its 2,4-dinitrophenylhydrazone, m. p. 175–179°, which showed no depression in melting point when mixed with isobutyraldehyde 2,4-dinitrophenylhydrazone. The formation of isobutyraldehyde, though unexpected may well be a degradation product of the expected vinyl alcohol. The dark solid which separated from the distillation residue was dissolved in benzene, treated with charcoal and crystallized by diluting with petroleum ether (b. p. 30–60°). There separated yellow needles of anthraquinone melting at 280–283°.

Summary

A keto–enol tautomerism involving a 1,7-shift of hydrogen exists between the 10-alkylideneanthrones and the corresponding 10-alkenylanthranols.

The unstable 10-alkenylanthranols, which are described for the first time, are characterized by their acetates and by their peroxides.

The hitherto puzzling instability of the alkylideneanthrones at atmospheric conditions is explained by their enolization and formation of enol peroxides, followed by breakdown of the peroxides into anthraquinone and aldehydes.

CHICAGO, ILL. RECEIVED JULY 26, 1945