[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, CALCO CHEMICAL DIVISION, AMERICAN CYANAMID COMPANY]

Study of the Aqueous Esterification of Anthrahydroquinones

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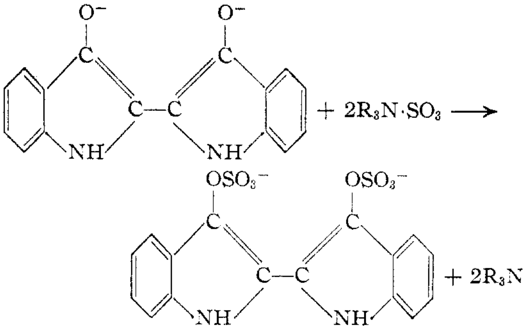
The aqueous esterification of anthrahydroquinones by means of tertiary amine-sulfur trioxide compounds in alkaline aqueous medium has been shown to lead to a disproportionation, with formation of anthraquinone and anthranol. Evidence is adduced to show that this disproportionation occurs through the intermediate anthrahydroquinone monosulfuric ester ion, and that sterically hindered α-substituted anthrahydroquinones show this reaction to a much greater degree than the unhindered β-substituted derivatives.

An interesting new reaction of wide applicability, the esterification of phenols in alkaline medium by means of certain tertiary amine-sulfur trioxide addition products, has been disclosed by our laboratory in several recently issued U. S. Patents.[1] In a later paper[2] the structure of these amine-sulfur trioxide compounds was discussed and their isomeric forms described.

A very valuable practical application of this general reaction of aqueous esterification of phenols, is found in the preparation of sulfuric ester salts of "leuco" vat dyes, as described in one of the above mentioned patents. During the study of this reaction we have made some interesting observations which we wish to report in the following article.

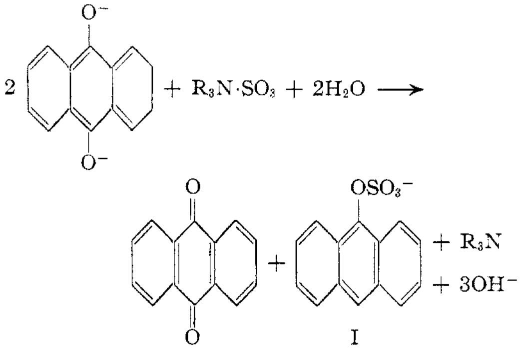
When the tertiary amine-sulfur trioxide compounds are treated with the "leuco" form of vat dyes of the indigoid, thioindigoid or condensed polycyclic quinone classes such as dibenzanthrone or anthanthrone, substantially the only product of reaction is the expected disulfuric ester, as illustrated in the case of indigo



(1)

We observed, however, that when this reaction was applied to those vat dyes which contain the 1,4-quinone structure characteristic of anthraquinone derivatives, an extensive side reaction occurred, which resulted in the regeneration of large amounts of quinone, while at the same time another ester of low water solubility appeared as a by-product.[3] These by-product esters differ from the normal disulfuric ester of the anthraquinone vat dye not merely in their low water solubility and lower content of sulfate groups, but also in the fact that they are incapable of regenerating the parent anthraquinone vat dye by the common procedure of acid hydrolysis and oxidation. In order to clarify this behavior, the reaction was carefully studied, choosing as model compound anthraquinone itself, because its reduction products are well described and easily identified.[4]

In the case of anthraquinone we were able to identify definitely the less soluble ester, formed as by-product, as the sulfuric ester of anthranol (I). The proportion of this by-product to oxidized anthraquinone in the final reaction mixture indicated a side reaction, occurring in parallel with the normal formation of disulfuric ester, and which is *in toto* a disproportionation



(2)

The more obvious explanations for this reaction, such as a further reduction of the anthrahydroquinone to anthranol by the aqueous sodium hydrosulfite, or a disproportionation of anthrahydroquinone itself (known to occur under certain conditions[5]) were eliminated experimentally. Also easily disproved was the possibility that the disulfuric ester of anthrahydroquinone might have been reduced to anthranol by hydrosulfite or by anthrahydroquinone.

For reasons discussed below, it seemed probable to us that the intermediate responsible for this disproportionation is the monosulfuric ester of anthrahydroquinone. We had already shown in this Laboratory that when hydroquinone is esterified by these $R_3N{\cdot}SO_3$ compounds in water, considerable amounts of its monosulfuric ester are formed even in the presence of an excess of esterifying agent, indicating that the second esterification is more difficult than the first. No doubt anthrahydroquinone monosulfuric ester is similarly formed from anthrahydroquinone. This monosulfuric ester, II, can be pictured in its ionized state by the resonance structures II-A and II-B.

Without implying the actual existence of these resonance structures, it is apparent that in structure II-B the sulfate radical is attached to a diphenylmethane carbon; the C–O bond of this radical should be quite weak, permitting ready cleavage

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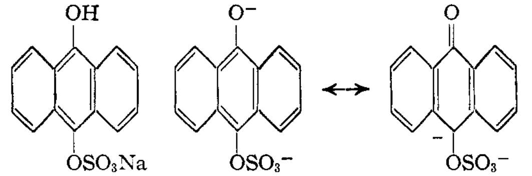
(1) H. Z. Lecher, M. Scalera and E. M. Hardy, U. S. Patents 2,396,582 and 2,402,647 (1946); H. Z. Lecher, M. Scalera and C. T. Lester, U. S. Patent 2,403,226 (1946).

(2) H. Z. Lecher and W. B. Hardy, THIS JOURNAL, **70**, 3789 (1948).

(3) Since preparation of this manuscript, a similar observation has been published by J. Taras (U. S. Patent 2,507,944), where the formation of a "different product" is mentioned, without elucidation of its properties or structure.

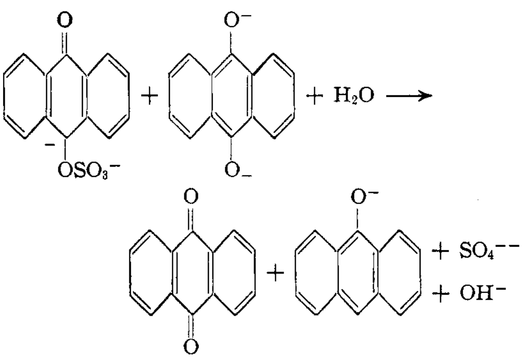
(4) J. Houben, "Das Anthracen und die Anthrachinone," Georg Thieme, Leipzig, 1929.

(5) K. H. Meyer, *Ann.*, **379**, 61 (1911).



II II-A II-B

by reducing agents. Thus with anthrahydroquinone the following reaction would be expected.

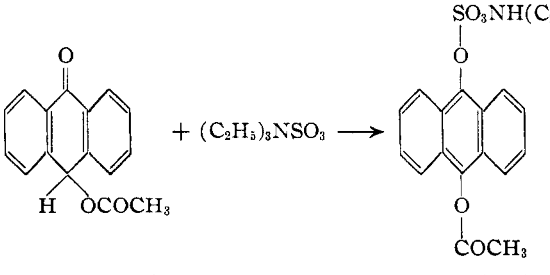


(3)

The anthranol thus formed is then esterified, by the excess of $R_3N\cdot SO_3$ present in the reaction mixture, to the observed anthranol sulfuric ester.

This hypothesis, which accounts for all products observed, has been confirmed experimentally by the preparation of the anthrahydroquinone monosulfuric ester II in the form of its acetyl derivative, and by the facile reaction of the latter with anthrahydroquinone in aqueous alkali, to produce anthraquinone and anthranol.

The synthesis of this product is reported in the patent literature[6] but work done in our laboratory failed to substantiate the patent claims.[7] We have found, however, that the acetyl derivative of II is formed in good yield by heating 10-acetoxyanthrone with molten triethylamine-SO_3 at 115° for a few minutes. This medium serves to bring about enolization and simultaneous sulfation



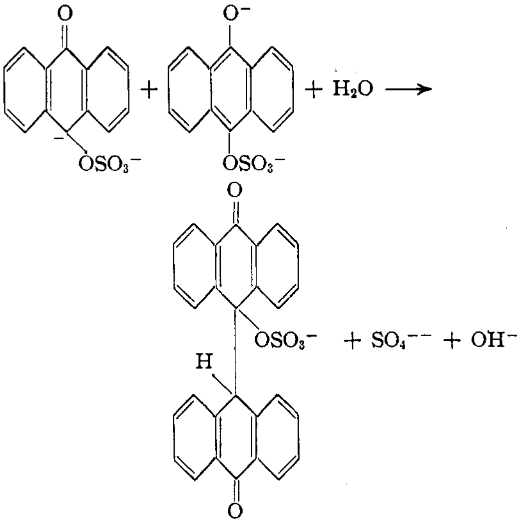
III

The reaction product, 10-acetoxyanthryl-9-triethylammonium sulfate (III) is a white solid, soluble in organic solvents with intense blue fluorescence, only slightly soluble in water, readily soluble to a yellow solution in aqueous alkali. Its alkaline solutions rapidly become turbid in the presence of air.

The free monosulfuric ester II itself is unstable, and attempts at isolating it in the pure state proved unsuccessful. Since it is well established that phenol sulfuric esters are stable in alkali[8] while aryl acetates are easily saponified, it can be safely assumed that II is formed as an unstable intermediate whenever its acetyl derivative is used in aqueous alkaline solutions. Compound III was used throughout in place of II in the study of the alkaline reactions described below.

Compound III was found to react rapidly with anthrahydroquinone in alkali, with immediate discharge of the red color, precipitation of anthraquinone, and formation of anthranol, according to equation (3). Compound III was also readily reduced by sodium hydrosulfite in alkali to produce anthranol. These results clearly confirm the role played by the monosulfuric ester II in the disproportionation reaction.

That equation (3) may be an over-simplification of the facts, however, was shown by a closer study of the properties of III. When treated with ammonia at 25°, or better with cold alkali in a nitrogen atmosphere, III furnished an excellent yield of a bimolecular product, IV, which can be pictured as resulting from arylation of the carbanion II-B by II-A[9]



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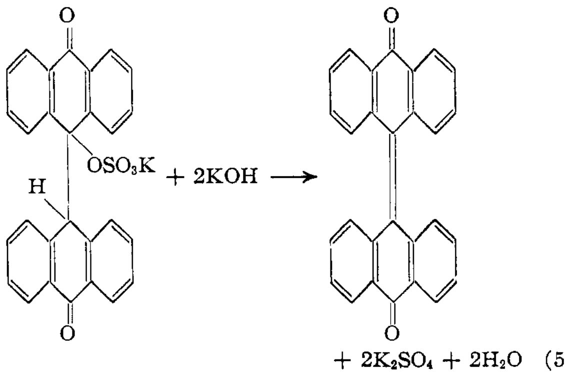
IV

This bimolecular ester IV reacts readily with potassium hydroxide solution at 90° forming 10,10'-bianthronylidene[10] in essentially quantitative yield



(5)

This reaction does not occur in carbonate solu-

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[6] German Patent 543,028; *Frdl.*, **18**, 1226 (1933).

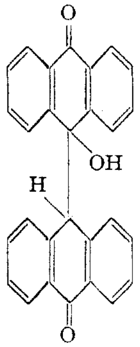
[7] Unpublished work carried out in our laboratory by Dr. A. W. Joyce.

[8] C. M. Suter, "Organic Chemistry of Sulfur," J. Wiley and Sons, Inc., New York, N. Y., 1944, p. 47.

[9] K. H. Meyer and A. Sander, *Ann.*, **396**, 143 (1913), have described an entirely analogous reaction, the formation of 10-bromobianthrone from 10-bromoanthrone in aqueous ammonia.

[10] H. Meyer, *Monatsh.*, **30**, 165 (1909).

tion, being an example of an elimination reaction in which the β-hydrogen atom is the first point of attack by the strong base. Compound IV is quite stable to acid hydrolysis at room temperature, confirming the alcoholic nature of the esterified hydroxyl group. Acid hydrolysis at higher temperature produces 10-hydroxybianthrone, a compound not before described, identified by analysis and by its chemical behavior on reduction

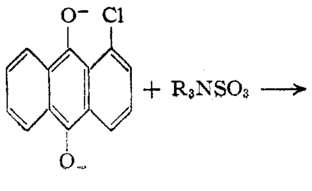


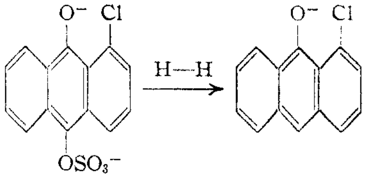
V

That this bimolecular ester IV may be actually an intermediate in the formation of anthranol from anthrahydroquinone monosulfuric ester is suggested by its facile reduction to anthranol by alkaline hydrosulfite.

The ionic character of the disproportionation reaction indicated in equation (3) is supported by the fact that the anthranol sulfuric ester I does not form when the esterification is carried out in anhydrous media. We were able to show that even in aqueous medium, the formation of anthranol can be greatly repressed or completely eliminated if the *p*H is maintained at a level sufficiently low to prevent ionization of the phenolic hydrogen (*p*H 8 to 9, instead of the *p*H 11 to 12, normal in "vatting" or hydrosulfite reductions). This observation, aside from its theoretical bearing on the present argument, has proved of great practical significance, since it has permitted the preparation of anthrahydroquinone disulfuric esters by an aqueous procedure with little or no by-product formation.

We have mentioned at the outset that the formation of the troublesome intermediate, anthrahydroquinone monosulfuric ester, is explained by the difference in reactivity toward sulfation between the hydroxyl groups of anthrahydroquinone and the unesterified hydroxyl in its monosulfuric ester. One would expect this difference to be greatly increased by the introduction of alpha substituents in the anthraquinone molecule. The *meso* hydroxyl next to a large alpha substituent is highly hindered sterically, and should make the monosulfuric ester more resistant to complete sulfation, and hence more prone to disproportionation





It is to be noted that by this mechanism, 1-chloroanthraquinone should give exclusively 1-chloro-9-anthrone, the unhindered hydroxyl group being the one more readily sulfated, and hence the only one subject to elimination. We proved experimentally that in the aqueous esterification of α-chloroanthraquinone, the reduced product consists of approximately 90% 1-chloro-9-anthrone, and 10% 1-chloro-10-anthrone.

Further experimental support of the mechanism given in equation (3) was secured from a study of this reaction with various substituted anthraquinones. This study is summarized in Table I. As expected, alpha substituents markedly increased the formation of anthranol even under the most favorable *p*H conditions.

The data in the table may indicate that effects other than steric ones (such as hydrogen bonding with the oxygen on the *meso* carbon, or electronic effects) play a secondary role in the enhancement of disproportionation. Thus it is noted that 1-benzoylamino-, 1-acetylamino- and 1-anilinoanthraquinone gave larger amounts of anthranol ester than the sterically larger 1-methyl-1-acetylamino-anthraquinone. Too close speculations based on these data are not warranted, however, since other factors of experimental technique (variable access of air, solubility differences, etc.) also affect the yields: the gross differences only have real significance. It is clear that beta substituents were found to have no effect. It is also interesting to observe that in those cases where the alpha substituent is part of a ring system, and therefore less free to interfere sterically (1,2-phthaloylcarbazole and 1,2-benzanthraquinone), the yields of the disulfuric ester are comparable to those obtained with unsubstituted or β-substituted anthraquinones.

Experimental

Experiment 1. Reduction and Esterification of Anthraquinone at High *p*H.—Sublimed anthraquinone (12.6 g., 0.06 mole) was stirred in 120 cc. of water under nitrogen; 12.8 g. (0.32 mole) of sodium hydroxide and 14.0 g. (0.08 mole) of sodium hydrosulfite were added. This slurry was stirred for one hour at 45–50°, cooled and treated with 16.0 g. (0.15 mole) of sodium carbonate and 21.6 g. (0.12 mole) of triethylamine-SO_3.[2] After three hours at 25–27°, most of the color was discharged and some solid had separated. Twenty-five cc. of 5 *N* sodium hydroxide was added, the triethylamine was removed with steam and the slurry was filtered. The precipitate, 5.9 g., 46% of the anthraquinone used, melted at 262–266° and gave a clear red vat characteristic of anthraquinone. A 2.0-g. sample recrystallized from toluene gave 1.6 g. of anthraquinone identified by m.p. and absorption spectrum. The filtrate was cooled to 10° depositing glistening plates which were filtered.

Anal. Calcd. for anthranol sulfuric ester, sodium salt, $C_{14}H_9O_4SNa$: C, 56.7; H, 3.04; S, 10.8; C/S, 14.0. Found: C, 52.6; H, 3.3; S, 9.84; C/S, 14.6.

Hydrolysis in dilute acetic acid at the boil gave a white solid, m.p. 159–164°, soluble in dilute hot alkali with yellow color, identified as anthranol.

The wet filter cake was redissolved in 75 cc. of water at 70°, treated with 10 cc. of 5 *N* triethylamine hydrochloride.

TABLE I

REDUCTION AND ESTERIFICATION OF SUBSTITUTED ANTHRAQUINONES AT LOW *p*H

Expt. No.	Anthraquinone derivatives	Recovered quinone, %	Anthranol ester, %	Anthrahydroquinone disulfuric ester isolated,[a] %
1	Anthraquinone[c]	11.1	None	88
2	2-Toluylanthraquinone[d]	17.7	None	79
3	1-Chloroanthraquinone[c]	23.0	22.2	45
4	1-Phenoxyanthraquinone[e]	22.0	20[b]	23
5	1-Anilinoanthraquinone[f]	28.0	33.3	20
6	N-Methyl-N-acetyl-1-aminoanthraquinone[g]	24.5	21.6	13
7	1-Acetylaminoanthraquinone[h]	34.6	26.3	10
8	1-Benzoylaminoanthraquinone[h]	41.2	33.3	5
9	1,2-Phthaloylcarbazole[i]	1.5	None	80
10	1,2-Benzanthraquinone[j]	Trace	None	88

[a] Because of the high solubility in water of the normal disulfuric esters of anthrahydroquinones, the per cent. isolated is in most cases in error on the low side. [b] Approximate yield only. [c] Plant intermediates, purified by crystallization. [d] 2-Toluylanthraquinone was obtained by the Friedel–Crafts reaction of anthraquinone β-carboxylic acid chloride with toluene (Schaarschmidt, *Ber.*, **48**, 831 (1915)). The crude product, obtained in 94% yield, m.p. 167–171° was recrystallized from boiling toluene to give pure material, m.p. 171–178° (reported 177–178°). [e] 1-Phenoxyanthraquinone was prepared by the procedure of German Patent 158,531. The crude product, m.p. 96–98°, was recrystallized from 10 parts toluene with charcoal; 68% was recovered as yellow crystals, m.p. 137–141° (reported 145°). [f] 1-Anilinoanthraquinone was prepared by the reaction of 1-chloroanthraquinone with aniline, following the procedure of Ullmann and Fodor, *Ann.*, **380**, 317 (1911). Recrystallized twice from alcohol, red crystals, m.p. 137–139°. *Anal.* Calcd.: C, 80.25; H, 4.38; N, 4.78. Found: C, 80.1; H, 4.41; N, 3.92. [g] N-Methyl-N-acetylaminoanthraquinone was prepared by acetylation of 1-methylaminoanthraquinone (technical recrystallized) with acetic anhydride by the procedure of German Patent 292,395; *Frdl.*, **13**, 400 (1923); silky yellow crystals, m.p. 214–215°, reported 213°. [h] Prepared by acylation of purified 1-aminoanthraquinone in nitrobenzene, respectively, with acetyl chloride (Graebe and Blumenfeld, *Ber.*, **30**, 1117 (1897), reports m.p. 215°; we found 212–216°) and with benzoyl chloride (Reverden, *Helv. Chim. Acta*, **1**, 209 (1917), reports m.p. 246°; we found 251–253°). [i] 1,2-Phthaloylcarbazole was prepared by the procedure of U. S. Patent 2,149,064. The product obtained in 66% yield was a yellow solid, m.p. 248–252°. *Anal.* Calcd.: C, 80.79; H, 3.72; N, 4.71. Found: C, 80.3; H, 3.37; N, 5.35. It was used without further purification. [j] 1,2-Benzanthraquinone was prepared by the procedure of Graebe (*Ann.*, **340**, 256 (1905)) (reported m.p. 160–166°, found 168°).

The white precipitate obtained, m.p. 135–138°, weighed 7.8 g., or 35% yield calculated as triethylammonium-9-anthryl sulfate. For positive characterization, see Experiment 2 below.

The filtrate after removal of the anthranol sulfuric ester sodium salt showed the strong blue fluorescence characteristic of the disulfuric ester of anthrahydroquinone, see Experiment 2 below. Oxidation with ferric chloride in acid solution at the boil regenerated anthraquinone.

Experiment 2. Identification of Anthranol Sulfuric Ester from Experiment 1. a. Esterification of Anthranol.—Nine and seven-tenths grams (0.05 mole) of pure anthranol was dissolved in 100 cc. of water and 25 cc. of ethyl alcohol by heating to 70° with the addition of 8.0 cc. (0.1 mole) of 50% sodium hydroxide. The clear yellow solution was cooled to 30°, 8.0 g. (0.075 mole) of sodium carbonate and 13.6 g. (0.075 mole) of triethylamine-SO_3 were added, and the mixture was stirred at 30° for 3.5 hours. The alcohol and triethylamine were distilled by steam and the slurry was filtered. There was recovered 3.2 g., 33% of unchanged anthranol, m.p. 156–157°. The yellow filtrate on cooling deposited yellow crystals which were filtered and washed with sodium chloride–sodium carbonate solution and dried. The weight was 9.9 g. Three grams of these crystals was hydrolyzed in an atmosphere of nitrogen with 50 cc. of 10% acetic acid at the boil. On cooling there was recovered 2.0 g. of anthrone, identified by m.p. Another 4.0 g. of the crystals was dissolved in water at 40° and to the clear solution was added 5 cc. of 5 *N* triethylamine hydrochloride solution. The separated crystals, 3.3 g., melted at 138–140° after recrystallization from water.

Anal. Calcd. for $C_{20}H_{25}NSO_4$: C, 64.2; H, 6.7; N, 3.8; S, 8.5. Found: C, 64.6; H, 6.7; N, 4.2; S, 8.3.

The mixed m.p. of this authentic material and the triethylamine salt of the less soluble sulfuric ester obtained from Experiment 1 above, was 134–138°.

b. Preparation of 9-Anthryl Benzoate for Identification.—Two grams of the sodium salt of the less soluble ester, described in Experiment 1 above, was treated with 4 cc. of benzoyl chloride with 20 cc. of pyridine for two hours at reflux. The resulting solution was drowned into dilute sodium hydroxide and the solid which separated on cooling was filtered, washed and recrystallized from ethanol to give 1.4 g. of a light yellow solid, m.p. 169–172°, reported 165°.[11] A mixed m.p. of this material with an authentic sample of 9-anthryl benzoate[11] was found to be 170–172°.

Experiment 3. Esterification of Hydroquinone.—Eleven grams (0.1 mole) of hydroquinone was dissolved in 100 cc. of water by means of 24.7 g. (0.44 mole) of potassium hydroxide, under exclusion of air. Forty-four and eight tenths grams (0.23 mol.) of N-ethylmorpholine-SO_3[12] was added. The mixture was stirred overnight at room temperature and filtered. The precipitate, 26.5 g., was a tan-colored solid largely contaminated with potassium sulfate. It was redissolved in about 150 cc. of water, the sulfate ions were removed with barium hydroxide solution and then the barium ions were removed with potassium carbonate solution. From the filtrate on salting there was isolated 10.5 g. of yellowish crystals, m. p. dec. 287–289°.

Anal. Calcd. for dipotassium hydroquinone disulfuric ester $C_6H_4S_2O_8K_2$: C, 20.8; H, 1.16; S, 18.5; K, 22.7. Found: C, 20.2; H, 1.1; S, 17.2; K, 24.0.

The filtrate was evaporated to small volume, diluted with ethanol, and clarified hot. There were obtained on cooling 3.5 g. of crystals which on recrystallization from alcohol gave a white solid, m.p. 225–230°.

Anal. Calcd. for monopotassium hydroquinone monosulfuric ester $C_6H_5SO_5K$: C, 31.5; H, 2.2; K, 17.1. Found: C, 30.6; H, 2.1; K, 18.3.

Experiment 4. Triethylammonium-9-(10-acetoxyanthryl) Sulfate (III).—10-Acetoxyanthrone was prepared by the reaction of potassium acetate with 10-bromoanthrone in acetic acid following the general procedure of K. H. Meyer.[13] In making larger size runs (up to 27 g. bromoanthrone) it was found advisable to mix the solutions of potassium acetate and bromoanthrone at 50° and then heat rapidly to reflux temperature. *Purification of the product* was performed by extraction with 13.5 parts of hot 80% aqueous alcohol and filtering off the solid deposited from the filtrate. The product was a light yellow solid melting at 103–105°; Meyer reports[13] 108° after recrystallization from hexane.

Thirty-seven grams (0.2 mole) of triethylamine-SO_3 was heated to 100° in an erlenmeyer flask to give a clear melt; 18.6 g. (0.074 mole) of 10-acetoxyanthrone was added and the melt was held at 110–115° for three minutes. The slurry was diluted with 140 cc. of ethylene chloride, clarified hot, and the white solid which crystallized out was filtered; yield 17.4 g. or 54%. The product appeared to melt momentarily at 160–170° but quickly resolidified as the result of decomposition. A 2.0-g. portion was recrystallized from 40 cc. of a 20% carbon tetrachloride solution in ethylene chloride with 65% recovery.

Anal. Calcd. for $C_{22}H_{27}NO_6S$: C, 60.9; H, 6.26; N, 3.24; S, 7.4. Found: C, 60.5; H, 6.60; N, 3.35; S, 7.6.

Triethylammonium-9-(10-acetoxyanthryl) sulfate (III) is

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(11) Padova, *Compt. rend.*, **143**, 121 (1906).

(12) W. B. Hardy, U. S. Patent 2,502,839 (1950).

(13) K. H. Meyer, *Ann.*, **379**, 66 (1911).

soluble in ethylene chloride, acetylene tetrachloride, slightly soluble in chlorobenzene and insoluble in hexane or carbon tetrachloride. Its solution in organic solvents shows strong blue fluorescence. It is slightly soluble in cold water with blue fluorescence. Addition of sodium hydroxide gives a yellow solution which quickly decomposes.

Experiment 5. Reduction of III with Hydrosulfite.—A solution of 4.8 g. (0.12 mole) of sodium hydroxide and 10.5 g. (0.05 mole real) of sodium hydrosulfite in 74 cc. of water was stirred in a nitrogen atmosphere at 50°. Two grams (0.0046 mole) of III was added uniformly during 2.5 hours. The nearly clear reaction mixture was stirred for half an hour longer and then 8.0 g. (0.095 mole) of sodium bicarbonate was added. The yellowish solid which precipitated was filtered, stirred in dilute alcoholic sodium hydroxide, and filtered again. The insoluble material, 0.0671 g. (7%) was shown by its reactions and m.p. to be anthraquinone. The yellow filtrate was acidified with acetic acid, the yellow slurry was boiled for a few minutes in the presence of a few drops of hydrochloric acid (color turned white, indicating ketonization). It was filtered and washed. The vacuum dried product weighed 0.667 g., 81% yield calculated as anthrone. The crude product melted at 148–154°. Recrystallized from 80% acetic acid, 77% recovery, m.p. 153–156°; it showed no depression in m.p. when mixed with an authentic sample of anthrone. The benzoyl derivative of the product, obtained in 74% yield, melted at 171–173° and did not depress the m.p. of 9-anthryl benzoate.[11]

Experiment 6. Reaction of III with Anthrahydroquinone. One gram (0.005 mole) of anthraquinone was vatted by stirring in a nitrogen atmosphere with 8 cc. of water, 1.2 g. (0.0052 mole) of sodium hydrosulfite and 43. cc. of 5 *N* sodium hydroxide for one-half hour at 50°. When the vatting was complete 2.0 cc. 5 *N* sodium hydroxide was added followed by 2.2 g. (0.005 mole) of III. An immediate reaction occurred, with formation of a yellow solid. After heating at 55° for three-quarters of an hour, 5 cc. of 5 *N* sodium hydroxide was added, the mixture was diluted with 25 cc. of water and filtered. The filtrate gave no more than a trace of precipitate upon acidification. Extraction of the wet filter cake with alcoholic alkali furnished 0.300 g. (31%) of anthrone, m.p. 152–157°. Extraction of the alkali insoluble portion with alkaline hydrosulfite followed by aeration furnished 0.56 g. (54%) of anthraquinone (m.p. 270–274°).

Experiment 7. Formation of Bimolecular Products from III. a. Hydrolysis of III with Ammonia: Formation of 10-Hydroxy-10,10′-bianthronyl Sulfate (IV).—Two grams (0.0046 mole) of III and 10 cc. of 28% aqueous ammonia were stirred at 30° in a nitrogen atmosphere for 15 minutes to give a slightly turbid orange solution. Complete hydrolysis occurred in this time as indicated by the absence of fluorescence in the solution. The reaction mixture was filtered into a solution of 4 g. of ammonium chloride and 10 g. of acetic acid in 20 cc. of water. The trace of oily material which formed was discarded and the solution was treated with 30 cc. of 5 *N* dibutylamine hydrochloride. The slightly yellow solid which precipitated was filtered off and washed with water to give 0.9 g. of wet cake. Seven-tenths gram of this cake dissolved in 15 cc. of methanol was treated with 5 g. of potassium acetate dissolved in 20 cc. of methanol. The white solid which formed weighed 0.4 g. dry. The yield calculated as hydroxybianthrone was 44%.

Anal. Calcd. for $C_{28}H_{18}KO_6S$: S, 6.15. Found: S, 5.94.

b. Hydrolysis of III with Alkali: Formation of 10-Hydroxy-10,10′-bianthronyl Sulfate (IV).—Six grams (0.0138 mole) of III was added to a solution of 7.5 g. (0.133 mole) of potassium hydroxide in 30 cc. of water; after stirring at 30° for three-quarters of an hour under nitrogen a nearly clear orange solution resulted. Thirteen and five-tenths grams (0.135 mole) of potassium bicarbonate was added, the solution was diluted with 250 cc. of water and clarified. Addition of 60 g. of potassium chloride to the filtrate deposited an oil. Crystallization was induced by stirring a portion of the oil with methanol and then seeding the main part with that which crystallized from methanol. The solid was filtered, and redissolved in 135 cc. of water, acidified to congo red, allowed to stand ten minutes at 25° and then clarified to remove a little flocculent material. The ester was salted out and crystallized as before. The salted product was washed with a 20% potassium chloride–2% potassium hydroxide solution. The vacuum-dried product weighed 4.0 g. The yield (based on real hydroxybianthrone content) was 88%.

Anal. Calcd. for $C_{28}H_{17}KO_6S$: C, 64.6; H, 3.27; S, 6.15; C/S, 28.0. Found: C, 50.3; H, 3.28; S, 4.73; C/S 28.3.

c. Formation of Bianthronylidene.—A 1.00-g. (0.0015 mole) sample of IV was heated for one hour at 90° in a solution of 5.0 g. (0.09 mole) of potassium hydroxide in 60 cc. of water stirred under nitrogen. The yellow solid weighed 0.5759 g., 100% yield, m.p. above 300°. It was identified as bianthronylidene by its properties and color reactions. This compound shows the interesting property of giving yellow solutions in acetylene chloride which become green on heating. The color change is reversible.[10]

Anal. Calcd. for $C_{28}H_{16}O_2$: C, 87.6; H, 4.2. Found: C, 86.6; H, 5.15.

When the potassium hydroxide in the above experiment was replaced by potassium carbonate only 4% hydrolysis (formation of insoluble product) occurred in one hour at 90°.

d. Formation of Hydroxybianthrone (V) **by Hydrolysis of IV.**—One gram (0.00149 mole real) of IV was hydrolyzed by heating in 50 cc. of 1 *N* hydrochloric acid for 15 minutes at 85° in a nitrogen atmosphere. The yellow solid obtained weighed 0.541 g. (95%). It sintered at 180° and melted at 219–249°.

Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.6; H, 4.5. Found: C, 83.1; H, 4.2.

Hydroxybianthrone, on recrystallization from ethylene chloride or benzene, gave a 35–50% recovery of anthraquinone, resulting from oxidation or dissociation. Extraction of the crude product with alcoholic alkali gave only a trace of alkali soluble material. Reduction of V, with sodium hydrosulfite and sodium hydroxide at 50°, followed by aeration and precipitation with sodium bicarbonate, gave an alkali-soluble and an alkali-insoluble fraction, which were separated by means of alcoholic alkali. The alkali-insoluble fraction (anthraquinone) accounted for 54% of the starting material; the alkali-soluble fraction (anthrone), corresponded to 32%.

Comparison of the hydrolysis rate of hydroxybianthrone sulfuric ester with that of anthranol sulfuric ester was made in the following manner. A 0.3000-g. sample (60% real) of the sulfuric ester of hydroxybianthrone was allowed to stand for 25 hours at 25° in 1.67 *N* hydrochloric acid in a nitrogen atmosphere. In this time 0.014 g. of insoluble material had formed indicating 7.8% hydrolysis. Under the same conditions the sulfuric ester of anthranol was 56% hydrolyzed.

Experiment 8. Reduction of IV to Anthranol.—An 0.800-g. (0.00138 mole) sample of IV was dissolved in 35 cc. of water; under nitrogen, the solution was treated with 2.0 g. (0.018 mole) of sodium carbonate and 1.0 g. (0.005 mole) of sodium hydrosulfite. The reaction mixture was heated at 60° for 15 minutes to give a yellow slurry. The product was filtered, washed and boiled in acid solution as described in Experiment 5 above. The dry product weighed 0.412 g. (93%). It sintered at 141° and melted at 148–157°. This material was identified as anthrone by mixed m.p. of a recrystallized sample and by conversion to 9-anthryl benzoate in 80% yield by reaction with benzoyl chloride in pyridine.

Experiment 9. Simultaneous Reduction–Esterification of Anthraquinone at Low *p*H.—A dispersed aqueous paste of anthraquinone (6.1 g., 0.03 mole real) was stirred with 27 cc. of water, 22.3 g. (0.21 mole) of sodium carbonate and 1.0 cc. of pyridine. After warming to 45° under nitrogen, 27.0 g. (0.15 mole) of triethylamine-SO_3 and 6.0 g. (0.033 mole) of sodium hydrosulfite were added, and the mixture stirred for three hours at 45–50°. To the smooth yellow slurry were added 80 cc. of 2.5 *N* sodium hydroxide and the triethylamine was removed by steam and air. The mixture was filtered hot. The insoluble material weighed 0.7 g., 11.1% of the anthraquinone used, and was identified as anthraquinone by m.p. and color reactions.

The filtrate was deep yellow with strong blue fluorescence. A portion treated with triethylammonium chloride gave no precipitate, indicating the substantial absence of anthranol sulfuric ester. It was salted at 50° with 10% potassium chloride, cooled to 5° and washed with 20% potassium chloride–5% sodium carbonate solution. The highly crystalline yellow product weighed 13.2 g. and analyzed (by acid oxidation) for 37.3% anthraquinone content, indicating a yield of 78%. An additional 10% yield was obtained by direct oxidation of the filtrate from the salting with ferric chloride. A portion of this salted product, recrystallized from potassium chloride solution, was submitted for analysis.

Anal. Calcd. for $C_{14}H_8O_8S_2K_2$: C, 35.2; H, 1.67; S, 13.4; C/S, 7.00. Found: C, 30.5; H, 2.5; S, 11.5; C/S, 7.06.

Experiment 10. Simultaneous Reduction–Esterification at Low *p*H—General Procedure.—This is illustrated by the experiments with 1-benzoylaminoanthraquinone (largely anthranol ester formed) and 2-toluylanthraquinone (largely normal disulfuric ester formed).

a. **1-Benzoylaminoanthraquinone.**—A dispersed paste of 1-benzoylaminoanthraquinone weighing 48.2 g. and containing 13.1 g. (0.04 mole) of pure product was stirred in a nitrogen atmosphere with 33.9 g. (0.32 mole) of sodium carbonate and 43.5 cc. of water. One cc. of dimethylaniline was added as catalyst, and the slurry was heated to 50°; 43.5 g. (0.24 mole) triethylamine-SO_3 and 9.3 g. (0.048 mole) of sodium hydrosulfite were added and the mixture was stirred for four hours at 50°. After adding 65 cc. of 20% sodium hydroxide the liberated triethylamine was distilled with steam, and the resulting slurry was diluted with 250 cc. of water and filtered hot. The insoluble material weighed 5.4 g., 41.2%, and was identified as unchanged 1-benzoylaminoanthraquinone. The filtrate on cooling deposited yellow crystals, 6.7 g. A small sample of this material was subjected to analysis after crystallization.

Anal. Calcd. for benzoylaminoanthranol sulfuric ester $C_{21}H_{14}O_4NSNa$: C, 47.9; S, 6.09; C/S, 21.0. Found: C, 48.2; S, 6.19; C/S, 21.0.

The bulk of the yellow crystals was subjected to acid oxidation. It yielded 62.3% of solid, accounting for 33.3% of the starting benzoylaminoanthraquinone as anthranol.

The filtrate, after removal of the anthranol ester, was salted with 20% by weight of potassium chloride, and the product resalted once again. Obtained 1.4 g., accounting for less than 5% of the original 1-benzoylaminoanthraquinone as disulfuric ester.

b. **2-Toluylanthraquinone.**—The reduction–esterification was carried out essentially as described under (a), using 15.8 g. (0.05 mole) of 2-toluylanthraquinone. After distillation of the triethylamine and hot filtration, the water-insoluble product was identified as unchanged 2-toluylanthraquinone: it accounted for 17.7% of the original usage. No crystals separated on cooling the solution to 10°. Upon adding 20% by weight of potassium chloride and cooling to 10°, a yellow solid separated which was filtered. After two reprecipitations from water by means of potassium chloride, the product weighed 25.0 g. and was shown by acid oxidation to contain 50% 2-toluylanthraquinone, corresponding to a yield of 79.1%. The product was submitted for analysis.

Anal. Calcd. for dipotassium salt of disulfuric ester of 2-toluylanthrahydroquinone $C_{22}H_{14}O_9S_2K_2$: C, 46.7; H, 2.49; S, 11.3; C/S, 11.0. Found: C, 40.3; H, 2.63; S, 9.84; C/S, 10.9.

Experiment 11. Preparation of the Isomeric 1-Chloroanthranol Sulfuric Esters. a. 1-Chloro-9-anthranol Sulfuric Ester.—Two and three-tenths grams (0.01 mole) of 1-chloro-9-anthrone[14] was stirred in 15 cc. of water, 0.2 cc. of dimethylaniline, 3.2 g. (0.03 mole) of sodium carbonate and 5.6 g. (0.03 mole) of triethylamine-SO_3 for two hours at 60° in a nitrogen atmosphere. After adding 10 cc. of 5 *N* sodium hydroxide the amine was distilled out. The mixture was diluted to 90 cc. and carbon dioxide was passed in until the slurry was no longer alkaline to phenolphthalein. The mixture was heated to 80° and filtered, using Filter-Cel. The ester was salted out with 40 g. of sodium carbonate from a volume of 200 cc. The product was washed with 10% sodium carbonate solution and dried to give 4.1 g. of a tan solid. Extraction with chloroform removed some solid which caused the sample to give a turbid solution.

Anal. Calcd. for $C_{14}H_8ClNaO_4S$: Cl, 10.7; S, 9.7; Cl/S, 1.0. Found: Cl, 9.35; S, 8.25; Cl/S, 1.02.

b. **4-Chloro-9-anthranol Sulfuric Ester.**—4-Chloro-9-anthrone[14] was esterified as described for the 1-chloro isomer. The yield of cream-colored solid was 75%.

Anal. Calcd. for $C_{14}H_8ClNaO_4S$: Cl, 10.7; S, 9.7; Cl/S, 1.0. Found: Cl, 8.40; S, 7.46; Cl/S, 1.02.

Experiment 12. Identification of the Disproportionation Product of 1-Chloroanthraquinone.—A dispersed paste of 1-chloroanthraquinone containing 14.6 g. (0.06 mole) was esterified with triethylamine-SO_3 essentially as described in Experiment 10. After adding excess alkali and distilling out the triethylamine the mixture was clarified at 90°. The water-insoluble material was unchanged 1-chloroanthraquinone (3.4 g., 23%). After cooling in the refrigerator the filtrate deposited 3.6 g. of light brown crystals. Further cooling of the filtrate yielded a second crop of 2.2 g. The combined materials accounted for 22.2% of the 1-chloroanthraquinone used.

Anal. Calcd. for $C_{14}H_8ClNaO_4S$: C, 51.0; S, 9.7; C/S, 14.0. Found: C, 38.3; S, 6.98; C/S, 14.6.

The balance of the 1-chloroanthraquinone was present as the leuco disulfuric ester, remaining in the filtrate, which upon oxidation furnished 6.6 g. of 1-chloroanthraquinone, or 45% of the starting material.

The mono-ester was identified as the ester of 1-chloro-9-anthranol as follows. A 0.5-g. sample was boiled in 6 cc. of acetic acid and 1.0 cc. of 5 *N* hydrochloric acid for 40 minutes. The vacuum dried product weighed 0.273 g., 99–106°. After two recrystallizations from acetic acid the product melted at 117–118° and did not depress the m.p. of 1-chloro-9-anthrone.[14]

A second esterification was made in the same manner as above again using 0.06 mole of 1-chloroanthraquinone. The less soluble fraction (anthranol ester), weighed 4.1 g. Comparison of this ester with mixtures of known composition of the sulfuric esters of 1-chloro-9-anthranol and 4-chloro-9-anthranol prepared as described above, by infrared analysis[15] showed this product to contain 90% of the ester of 1-chloro-9-anthranol.

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[14] E. D. Barnett and M. A. Matthews *J. Chem. Soc.*, 2553 (1923).

[15] Infrared work was carried out by Dr. D. N. Kendal of the Application Research Department of the Calco Chemical Division.