704. *Sulphuric Esters of Polycyclic Quinols.*

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Salts of the disulphuric esters of quinol, anthraquinol, 6 : 12-dihydroxy-anthanthrene, and 3 : 8-dihydroxy-1 : 2-6 : 7-dibenzopyrene have been prepared and studied. None undergoes replacement of the groups $^-O\cdot SO_3^-$ with the nucleophilic agents studied, but all are readily hydrolysed by acids and oxidised to the related quinones with acid oxidants.

ALTHOUGH many of the sulphuric esters of quinols have become important technically, because of the ease with which they are oxidised to the parent quinones,[1] little has been published about their general chemistry. Their preparation generally involves acylation of a quinol [2] or reduction of a quinone in the presence of an acylating agent,[3, 4, 5] and both methods have been used in the present work.

The sulphuric esters are known to be unstable in light [6] or in acid solution, and most are readily soluble in water and difficult to purify. The present investigation was concerned mainly with the sodium and potassium salts of the di-*O*-sulphuric esters of anthraquinol (I), 6 : 12-dihydroxyanthanthrene (II), and 3 : 8-dihydroxy-1 : 2-6 : 7-dibenzopyrene (III). These were prepared by reduction of the corresponding quinones with iron powder in pyridine in the presence of chlorosulphonic acid, essentially by the method already described,[3] and were best purified by crystallisation from water, which generally gave hydrates. The corresponding barium salts were more sparingly soluble in water and unstable. The disodium salt of the di-*O*-sulphuric ester of *leuco*indigotin has been obtained both as decahydrate [1] and tetrahydrate.[7]

(I)   (II)   (III)

The sodium salts were reduced to the corresponding aromatic hydrocarbon in 10—20% yield on being shaken in alcohol suspension with Raney nickel.[8] Each gave the quinone on oxidation with aqueous ferric chloride or nitrous acid. When chlorine- or bromine-water, acidified hydrogen peroxide (with or without ferrous sulphate), or potassium persulphate was used the product contained a small proportion of phenolic compounds. With the anthracene derivative (I) the principal phenolic product had almost the same absorption spectrum in concentrated sulphuric acid as 2-hydroxyanthraquinone; a smaller proportion of 1-hydroxyanthraquinone was formed also. The anthanthrene derivative (II) gave a phenolic product which differed from the known 3 : 9-dihydroxyanthranthrone [9] and was not an *o*-hydroxycarbonyl compound. The salts did not show any simple reaction with such nucleophilic reagents as aniline, potassium cyanide, potassium ethoxide, or

[1] Bader, *Chimie et Industrie*, 1924, Nos. 449, 445.
[2] Baumann, *Ber.*, 1878, **11**, 1907; Verley, *Bull. Soc. chim. France*, 1901, **25**, 46; Scalera, Hardy, Hardy, and Joyce, *J. Amer. Chem. Soc.*, 1951, **73**, 3094; U.S.P. 403,226.
[3] Jones, Wylam, Morton, and Morton Sundour Fabrics, B.P. 245,587, 248,802, 251,491.
[4] Coffey, *Chem. and Ind.*, 1953, 1068; B.P. 633,408.
[5] G.P. 489,725, 520,031.
[6] Gerhard and Dierkes, *Rayonne et Fibres*, 1953, **9**, No. 4, 43; B.P. 734,932.
[7] Ruggli and Stauble, *Helv. Chim. Acta*, 1940, **23**, 689.
[8] Cf. Jain, Mittel, and Seshadri, *J. Sci. Ind. Res., India*, 1953, **12**, B, No. 12, 647.
[9] Bradley and Waller, *J.*, 1953, 3778.

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potassium benzoate. In this they resembled sodium phenyl sulphate [10] rather than sodium methyl sulphate, although the first reacts with sodium phenoxide in liquid ammonia to form diphenyl ether,[11] and potassium phenyl sulphate affords phenyl benzoate with potassium benzoate.[12] The potassium salt of (I) showed no tendency to react with bromine or ferric chloride in benzene. All the salts were notably stable towards hot aqueous alkalis but were decomposed on the addition of acid to their aqueous solutions.[13] From boric acid and a suspension of the salt (I; $R = SO_3Na$) in aniline, heated rapidly to the boiling point, 9 : 10-dianilinoanthracene was readily formed : Liebermann [14] obtained the same product similarly from 9 : 10-diacetoxyanthracene.

When anhydrous the salts were unexpectedly stable to heat in the absence of air, but decomposition occurred rapidly when both air and moisture were present. The salts were relatively stable towards alkaline oxidants but acid oxidants changed them into the related quinones at rates which greatly exceeded the rates of hydrolysis in the absence of oxidising agents. Bader [1] considered that in acid oxidation hydrolysis of both sulphate groups occurred, the quinol so formed being an essential intermediate. Later he held that oxidation occurred directly and that hydrolysis was not involved.[15] Another view of the reaction suggests that in the presence of hydrogen peroxide hydrolysis of one sulphate group occurs first, the resulting phenol being oxidised through a radical; [16] this accords better with the present results.

The importance of the monosulphates as intermediates in the acid oxidation of the disulphates of quinols is evident from two considerations. Rapid oxidation to the related quinone does not take place except in the presence of an effective (acid) hydrolytic agent. Neither free monosulphate nor free quinol can be detected in the presence of nitrous acid though in the absence of this the presence of the monosulphate can be demonstrated. 10-Hydroxy-9-anthryl hydrogen sulphate (as IV) which was used in these experiments was not isolated. It was prepared from oxanthrone acetate by reaction with triethylamine–
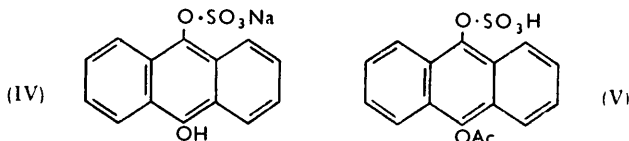
sulphur trioxide and hydrolysis of the resulting salt of 10-acetoxy-9-anthryl hydrogen sulphate (V) in alkaline solution. Parallel experiments with corresponding derivatives of quinol showed that phenols were more easily oxidised than their disulphates when the oxidant was nitrous acid in dilute sulphuric acid. Neither the diacetate nor the disulphate of quinol was changed on brief contact at 60° while the monoacetate and monosulphate were both oxidised. Experiments with potassium phenyl sulphate showed that the rate of hydrolysis of this with hydrochloric acid was not affected by the addition of hydrogen peroxide. The rate was, however, dependent on the medium, increasing in the series, water < water–alcohol (15 : 85 v/v) < water–acetone (34 : 66 v/v) < acetone.

EXPERIMENTAL

Disodium 9 : 10-*Anthrylene Disulphate* (I; $R = SO_2Na$).—Pyridine (50 g.) and chloro-sulphonic acid (10 g.) were mixed below 20°, then heated to 60°. Anthraquinone (6 g.) and iron powder (4 g.) were added and the reactants were vigorously shaken at 60—70° for 3 hr. The resulting suspension was added to water (300 c.c.) containing sodium carbonate (15 g.),

[10] Burkhardt, Ford, and Singleton, *J.*, 1936, 17.
[11] Kranzfelder and Sowa, *J. Amer. Chem. Soc.*, 1937, **59**, 149.
[12] Czapek, *Monatsh.*, 1914, **35**, 637.
[13] Burkhardt and Lapworth, *J.*, 1926, 684.
[14] Liebermann, *Annalen*, 1934, **513**, 157.
[15] Bader, *Amer. Dyestuff Reporter*, 1938, **27**, 455.
[16] Ainsworth and Johnson, *J. Soc. Dyers and Colourists*, 1955, **71**, 592.

pyridine was removed in steam under reduced pressure, and the residual suspension was heated to 80° and then filtered, the residue being washed with a small volume of hot water. On the addition of salt to the combined filtrates to give a 10% solution of sodium chloride, pale yellow plates separated; these were collected and dried in a vacuum-desiccator (yield 11 g.). The use of a coarser grade of electrolytic iron in this preparation gave a slower reaction, and the best yields were obtained when the steam-distillation was carried out on a succession of small portions to avoid decomposition of the disulphuric ester.

The crude disodium salt (30 g.) was purified by dissolution at 90° in water (150 c.c.) containing a few drops of aqueous sodium hydroxide (charcoal), giving pale yellow plates. Disodium 9 : 10-anthrylene disulphate is very soluble in water to a pale yellow solution with an intense blue fluorescence. On addition of nitric acid, or sodium nitrite and acetic acid, anthraquinone, m. p. and mixed m. p. 281°, was precipitated in an almost pure form. Samples of the disodium salt which had been kept for 24 hr. over calcium chloride in an evacuated desiccator consisted of a *tetrahydrate* [Found : Na, 9·2; SO_4, 39·8; anthraquinone, 42·3. $C_{14}H_8(O\cdot SO_3Na)_2,4H_2O$ requires Na, 9·5; SO_4, 39·5; anthraquinone, 42·8%].

On the addition of an excess of dilute sulphuric acid to an aqueous solution of the disodium salt the blue-violet fluorescence increased in intensity. After short heating of the acidified solution at 60° in the absence of air, addition of an excess of dilute sodium hydroxide caused development of a yellow colour and a brick-red fluorescence in ultraviolet light (sodium 10-hydroxy-9-anthryl sulphate).

Dipotassium 9 : 10-Anthrylene Disulphate (I; $R = SO_3K$).—Excess of barium acetate was added to a solution of the disodium salt (5 g.) in water (100 c.c.). The salt which separated was collected, washed with barium hydroxide solution, then added to a hot solution of sufficient potassium sulphate to ensure precipitation of barium. Barium sulphate was removed, potassium chloride was added to the filtrate, and the dipotassium salt which separated in plates on cooling was recrystallised twice from water containing a small amount of potassium hydroxide. After being dried over calcium chloride in a vacuum-desiccator the resulting salt was a *dihydrate* [Found : loss at 80° *in vacuo*, 7·4; anthraquinone formed on oxidation, 42·5. $C_{14}H_8(O\cdot SO_3K)_2,2H_2O$ requires H_2O, 7·7; anthraquinone, 41·1%].

Disodium Anthanthren-6 : 12-ylene Disulphate (II, $R = SO_3Na$).—Prepared from anthanthrone (18 g.), chlorosulphonic acid (20 g.), pyridine (100 g.), and iron powder (4 g.) as described for the anthracene analogue, except that the amount of sodium carbonate used was 45 g., the crude disodium salt separated as bronze plates (70%). Two further crystallisations from water rendered just alkaline and subsequent drying in air gave the disodium salt as a yellow-brown *tetrahydrate* [Found : loss at 70° *in vacuo*, 12·4; SO_4, 31·8; 31·8, 32·0; anthanthrone formed on oxidation, 52·2, 52·6, 52·4. $C_{22}H_{10}(O\cdot SO_3Na)_2,4H_2O$ requires H_2O, 12·3; SO_4, 32·8; anthanthrone, 52·4%].

Disodium 1 : 2-6 : 7-Dibenzopyren-3 : 8-ylene Disulphate.—The dibenzopyrenequinone employed in this preparation was prepared by the action of benzoyl chloride on *meso*benzanthrone. When the quinone (18 g.) was treated with pyridine (108 g.), chlorosulphonic acid (22 g.), and iron powder (8 g.) at 60° for 4 hr., and the product was isolated as for the anthracene analogue, small orange crystals of disodium 1 : 2-6 : 7-dibenzopyren-3 : 8-ylene disulphate separated. Recrystallisation from water made just alkaline with sodium hydroxide gave the salt as an orange *dihydrate* [Found, in hydrated salt : H_2O, 5·48. $C_{24}H_{12}(O\cdot SO_3Na)_2,2H_2O$ requires H_2O, 6·25%], and this, on being heated in a vacuum drier at 100°, gave the yellow, anhydrous salt which deliquesced in air. The yellow aqueous solution showed a blue-green fluorescence ($\lambda_{max.}$ 390 and 480 mμ).

9-Toluene-p-sulphonyloxyanthracene.—Toluene-*p*-sulphonyl chloride (1·5 g.) was heated on a water-bath with a solution of anthrone (1·0 g.) in pyridine (2·5 c.c.); after 2 min. solidification occurred and was soon complete. Water (25 c.c.) was added, the whole was shaken, and the solid which separated was collected, and washed with dilute sodium hydroxide solution, and finally with water. Purification from alcohol gave the colourless *derivative*, m. p. 167—168° (Found : C, 72·7; H, 4·4; S, 9·05. $C_{21}H_{16}O_3S$ requires C, 72·4; H, 4·6; S, 9·2%).

Reduction Experiments.—(1) A solution of 9-toluene-*p*-sulphonyloxyanthracene (0·4 g.) in absolute alcohol (200 c.c.) was shaken overnight with a suspension (4 c.c. of settled suspension prepared by Vogel's method) of Raney nickel in alcohol. The resulting solid was collected and washed with benzene, and the benzene and alcohol solutions were combined and shaken with water (1 l.). The benzene layer which was formed was separated, washed, evaporated to

small volume, mixed with light petroleum (b. p. 60—80°; 150 c.c.), and chromatographed on alumina. Elution with light petroleum removed coloured material, and further treatment with benzene–light petroleum gave anthracene as colourless, blue-fluorescent plates, m. p. and mixed m. p. 209—212°.

(2) Dipotassium 9 : 10-anthrylene disulphate (0·5 g.), suspended in absolute alcohol (200 c.c.), was similarly reduced with Raney nickel (3 c.c. of alcoholic suspension); anthracene, m. p. 213° (0·036 g.), resulted. When the reactants were refluxed for 3 hr. instead of being shaken overnight the yield of anthracene was 0·041 g. Anthraquinone was also readily reduced in alcohol with Raney nickel but no anthracene could be isolated.

(3) Disodium anthanthren-6 : 12-ylene disulphate (0·5 g.) was shaken for 15 hr. with a suspension (3 c.c.) of Raney nickel in alcohol. The reactants exhibited an intense blue-green fluorescence and this was not changed during the reaction. The product was isolated substantially as with the anthracene derivative. The benzene-soluble part of the product was isolated and then chromatographed on alumina from light petroleum (b. p. 100—120°). The yellow band which formed was extracted with benzene affording yellow plates (0·04 g.). Refluxing the reactants for 3 hr. instead of shaking them gave the same product (0·08 g.). The products from the two preparations were combined and crystallised from benzene (20 c.c.); yellow plates of anthanthrene were obtained, having m. p. 261° alone or when mixed with the compound prepared by reduction of anthanthrone with hydriodic acid.[17] On being shaken with an alcohol suspension (3 c.c.) of Raney nickel in absolute alcohol (250 c.c.), anthanthrone (0·3 g.) gave 6 : 12-dihydroxyanthanthrene (violet coloration on the addition of sodium hydroxide solution) but no anthanthrene.

(4) Similar reduction of disodium 1 : 2-6 : 7-dibenzopyren-3 : 8-ylene disulphate (0·5 g.) by shaking overnight with Raney nickel in alcohol (3 c.c.) and isolation of the product as for the anthanthrene derivative gave yellow leaflets (0·02 g.) of 1 : 2-6 : 7-dibenzopyrene, m. p. 310°, alone or when mixed with the compound prepared by reduction of 1 : 2 : 6 : 7-dibenzopyrene-3 : 8-quinone with zinc dust, zinc chloride, and sodium chloride [18] (Found : C, 95·0; H, 4·65. Calc. for $C_{24}H_{14}$: C, 95·4; H, 4·6%).

Action of Heat on Salts of 9 : 10-*Anthrylene Dihydrogen Disulphate.*—(a) *Disodium salt.* On being heated rapidly to 90° in an acid-free atmosphere the tetrahydrate decomposed forming a green product; no sulphite ions could be detected. The green material dissolved in dilute sodium hydroxide with the deep red colour of anthraquinol. A solution containing 2 g. in warm 5% aqueous sodium hydroxide (100 c.c.) was aerated until the red colour disappeared. The resulting suspension was boiled, then filtered from anthraquinone, and the filtrate was acidified. The precipitate was crystallised from acetic acid, chromatographed on alumina, and treated with dilute sodium hydroxide solution. The following compounds were isolated : naphthadianthrone ($\lambda_{max.}$ in concentrated sulphuric acid, 512, 575; Brockmann [19] records 512, 537, 575 mμ); 10 : 10′-dianthronyl, m. p. 245°, giving a yellow green solution in concentrated sulphuric acid which was changed to red on being warmed; [20] dianthronol, m. p. 230°, giving a yellow fluorescent solution in benzene which became greener on being warmed, and a Bordeaux solution in concentrated sulphuric acid.[21]

Decomposition of the salt was greatly hastened by acid; even sodium hydrogen sulphate caused rapid decomposition at 65°. Heated in a vacuum the salt was much more stable.

(b) *Dipotassium salt.* The anhydrous salt was stable in air at 80°, and even at 100° decomposition was slight after 6 hr.; the product contained anthraquinone. Decomposition was still slow at 70° even after the salt had been mixed with potassium hydrogen sulphate. In a vacuum the salt changed little below 200°. At 200—220° decomposition was complete in 2 hr.; sulphur dioxide was present. In a further experiment the salt (1 g.) was heated to decomposition at 230—240° in a vacuum, the containing vessel was cooled, and boiled-out aqueous potassium hydroxide (1 g. in 70 c.c.) was admitted. The resulting suspension was shaken and filtered, and the filtrate was added to 0·1N-iodine (50 c.c.). Back-titration with sodium thiosulphate solution showed that the product contained 0·066 g. of sulphur dioxide. Recrystallisation of the alkali-insoluble part (0·44 g.) gave anthraquinone. The alkali-insoluble

[17] Scholl and Meyer, *Ber.*, 1934, **67**, 1229.
[18] Clar, *Ber.*, 1939, **72**, 1645.
[19] Brockmann, *Annalen*, 1942, **553**, 1.
[20] Clar and Muller, *Ber.*, 1930, **63**, 869.
[21] Meyer, *Ber.*, 1909, **42**, 143.

part (0·39 g.) obtained in a similar experiment gave anthraquinone, m. p. 281° (0·21 g.) and m. p. 277° (0·08 g.). The anhydrous potassium salt was stable to heat at 150° *in vacuo* with potassium hydrogen sulphate.

(c) *Salts of anthanthren-6 : 12-ylene dihydrogen disulphate.* The hydrated sodium salt was stable at 80° in air; above 90° decomposition occurred slowly. In the absence of air decomposition occurred at 150°, sulphur dioxide and 6 : 12-dihydroxyanthanthrene being formed. The anhydrous potassium salt was stable in air at 100°; above this temperature decomposition occurred. In the absence of air the salt was stable below 200°.

(d) *Disodium* 1 : 2-6 : 7-*dibenzopyren-3 : 8-ylene disulphate.* This was stable in air at 90° for 1·5 hr. In the absence of air the yellow anhydrous salt was formed first, then decomposed at ~160°, sulphur dioxide being liberated.

Action of Nucleophilic Agents on the Salts.—(1) *Aniline.* (a) With aniline (30 c.c.) at 100° for 3 hr. anhydrous dipotassium 9 : 10-anthrylene disulphate (1 g.) was unchanged. Refluxing for 15 min. decomposed the salt completely, forming anthraquinone in small amount and an unidentified red product; the same result was obtained after 3 hr. at 150°. No 9 : 10-dianilinoanthracene was formed in these experiments. When the salt (2 g.) was refluxed for 10 min. with aniline (10 c.c.) and boric acid (3 g.) a red solution resulted which contained 9 : 10-dianilinoanthracene. This was isolated by addition of the cooled product to 5% hydrochloric acid (150 c.c.), separation of the solid which formed, washing with methanol, extraction of a small proportion of anthraquinone with alkaline dithionite solution, and crystallisation of the insoluble part from xylene. The resulting yellow plates had m. p. 295—300°, alone or when mixed with 9 : 10-dianilinoanthracene prepared by Liebermann's method.[14]

(b) Dipotassium 1 : 2-6 : 7-dibenzopyren-3 : 8-ylene disulphate (4 g.) and aniline (15 c.c.) on being heated slowly to 150° and then kept for several hr. at this temperature gave 1 : 2-6 : 7-dibenzopyrene-3 : 8-quinone, but no nitrogen-containing derivative.

(2) *Potassium cyanide.* Dipotassium 9 : 10-anthrylene disulphate (1 g.) and potassium cyanide (1 g.) in water (40 c.c.) were heated at 125° for 3 hr. in a sealed tube. On being cooled the solution had a pale yellow colour and a few needles were present. Heating was continued at 140° for 6 hr. The cooled product contained much unchanged dipotassium salt; the needles which separated were anthraquinone. 9 : 10-Dicyanoanthracene [22] was absent.

(3) *Sodium ethoxide.* No reaction occurred when dipotassium 9 : 10-anthrylene disulphate (1 g.), sodium ethoxide (10 g.), and absolute alcohol (40 c.c.) were shaken together for 24 hr. When the same reactants were refluxed for 2 hr. a small amount of benzene-soluble material resulted but there was no indication of the presence of 9 : 10-diethoxyanthracene.[23]

Salts of 10-Acetoxy-9-anthryl Hydrogen Sulphate.—The triethylamine salt (Found : S, 7·1. Calc. for $C_{22}H_{27}O_6NS$: S, 7·4%) was prepared by Scalera, Hardy, Hardy, and Joyce's method.[2] A yellow colour developed (hydrolysis of acetyl group) on the addition of sodium hydroxide to its colourless solution in water. In this instability towards alkalis triethylammonium 10-acetoxy-9-anthryl sulphate differs from dipotassium 9 : 10-anthrylene disulphate. Solutions of both salts fluoresce blue in ultraviolet light, and that of the disulphate remains unaffected by the addition of sodium hydroxide whilst that of the 10-acetoxy-derivative changes to brick-red. Neither of the derivatives is immediately affected by the addition of an excess of dilute sulphuric acid and both readily yield anthraquinone on the further addition of sodium nitrite.

Potassium p-Hydroxyphenyl Sulphate and Dipotassium p-Phenylene Disulphate.—A solution of quinol (20 g.) in the minimum volume of pyridine was added to one of chlorosulphonic acid (21 g.) in pyridine (160 c.c.). The temperature was raised slowly to 65° and kept thereat for 3 hr., access of air being prevented. The resulting solution was added to water containing potassium hydroxide (45 g.), and pyridine was removed under reduced pressure. The filtered solution afforded large straw-coloured crystals on being cooled; recrystallisation from water gave the pure *dipotassium p-phenylene disulphate*, m. p. 287° (Found : C, 20·7; H, 1·1; S, 18·4; K, 22·8. $C_6H_4O_8S_2K_2$ requires C, 20·8; H, 1·2; S, 18·3; K, 23·2%). Salt was added to the mother-liquor to complete the precipitation and, after filtration, the mother-liquor was evaporated to dryness under reduced pressure and the residue extracted with hot 95% alcohol. On being cooled the extract gave brown crystals (14 g.), which gave colourless *potassium p-hydroxyphenyl sulphate* (6 g.), m. p. 220° (from alcohol) (Found : C, 31·4; H, 2·3; S, 14·0; K, 17·4. $C_6H_5O_5SK$ requires C, 31·6; H, 2·2; S, 14·0; K, 17·1%).

[22] Beyer and Fritsch, *Ber.*, 1941, **74**, 494.
[23] Meyer, *Annalen*, 1911, **379**, 37.

Hydrolyses.—Effect of solvent on the rate of hydrolysis of sulphates. (1) Potassium phenyl sulphate (Found : C, 33·9; H, 2·7; S, 15·0; K, 18·2. Calc. for $C_6H_5O_4SK$: C, 33·9; H, 2·4; S, 15·0; K, 18·0%) was prepared by the action of chlorosulphonic acid on phenol in pyridine, the resulting phenyl hydrogen sulphate being converted into the potassium salt. 0·25N-Hydrochloric acid (10 c.c.) was added to an 0·1M-solution of potassium phenyl sulphate in (a) water (50 c.c.), (b) a mixture (50 c.c.) of water (1 vol.) and acetone (4 vols.) at 50° ± 0·2°. At intervals, volumes (10 c.c.) were withdrawn and titrated against 0·1N-sodium hydroxide (*p*-nitrophenol as indicator). Results were :

Time (hr.)		0	1	2	4	12	23
0·1N-NaOH required (c.c.)	(a)	4·0	4·1	4·2	4·45	5·2	6·4
	(b)	4·0	9·0	10·5	11·6	12·2 *	—

* Hydrolysis complete.

(2) 0·25N-Hydrochloric acid (10 c.c.) was heated at 50° ± 0·2° with (a) a 0·1M-solution (50 c.c.) of potassium *p*-hydroxyphenyl sulphate in water, (b) a 0·1M-solution (50 c.c.) of the same salt in acetone, and (c) a 0·05M-solution (50 c.c.) of dipotassium *p*-phenylene disulphate in water. Neutralisation (*p*-nitrophenol) of 10 c.c. of the solution required the stated volumes of alkali at the times recorded.

Time (hr.)		0	0·0833	1·0	2·0	3·0	6·0	19·0	22·0
0·1N-NaOH required (c.c.)	(a)	4·0	4·0	4·1	—	4·2	4·3	—	5·0
	(b)	4·0	4·2	—	10·7 *	—	—	—	—
	(c)	4·0	4·0	4·2	4·3	—	4·75	6·0	—

* $KHSO_4$ precipitated.

Oxidation of Disodium 9 : 10-*Anthrylene Disulphate with Hydrogen Peroxide and Hydrochloric Acid. Formation of 2-Hydroxyanthraquinone.*—Concentrated hydrochloric acid (10 c.c.) and 60-vol. hydrogen peroxide (40 c.c.) were added to a solution of the disodium salt (8 g.) in water (190 c.c.). After several hr. at 65° the reactants afforded a yellow precipitate (3·7 g.). (a) This was dissolved in toluene and the resulting solution was extracted with hot dilute aqueous sodium hydroxide containing 5% of alcohol. The bright red alkaline solution was boiled, treated with charcoal, and filtered. On being acidified the filtrate gave a bright yellow solid (0·23 g.) which had m. p. 305° after crystallisation from toluene. Its solution in concentrated sulphuric acid showed maximum absorption at 250, 290, 324, 414, and 490 mμ. (Meyer and Fischer [24] report maxima at 290, 320, 410, and 500 mμ for 2-hydroxyanthraquinone.) (b) In a second experiment the yellow precipitate was dissolved in toluene and chromatographed on alumina. Anthraquinone passed quickly through the column, leaving two bands which were separated and extracted with alcoholic hydrochloric acid. The extract was evaporated and the residue sublimed in a vertical tube; two bands were formed. The lower yellow band, the bulk of the adsorbed material, consisted of 2-hydroxyanthraquinone. The red upper band afforded 1-hydroxyanthraquinone, m. p. 186°, which gave a positive boroacetate test and a sparingly soluble, magenta barium salt. There was no indication of hydroxylation when finely divided anthraquinone was heated at 70° for 8 hr. with hydrochloric acid and hydrogen peroxide, or when disodium 9 : 10-anthrylene disulphate was heated with hydrogen peroxide in the absence of acid. Hydroxylation occurred, however, when the oxidant was hydrogen peroxide with acetic acid, or potassium persulphate with acetic acid, and rapidly when the oxidant was bromine-water, chlorine-water, or hydrogen peroxide–acetic acid–ferrous sulphate.

In parallel experiments with disodium anthanthren-6 : 12-ylene disulphate (4 g.) in water (100 c.c.), concentrated hydrochloric acid (5 c.c.) and 60-vol. hydrogen peroxide (20 c.c.) brick-red material separated from solution. A portion of this dissolved sparingly in dilute sodium hydroxide forming a blue solution, from which a small amount of a flocculent red precipitate was formed on acidification. The boroacetate test was negative.

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[24] Meyer and Fischer, *Ber.*, 1913, **46**, 90.