ratio of the equilibrium constant of the undissociated tautomers to the constant for the completely ionized substances is equal to the ratio of the dissociation constants of the two hydroxy quinones.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

2-HYDROXY-1,4-ANTHRAQUINONE

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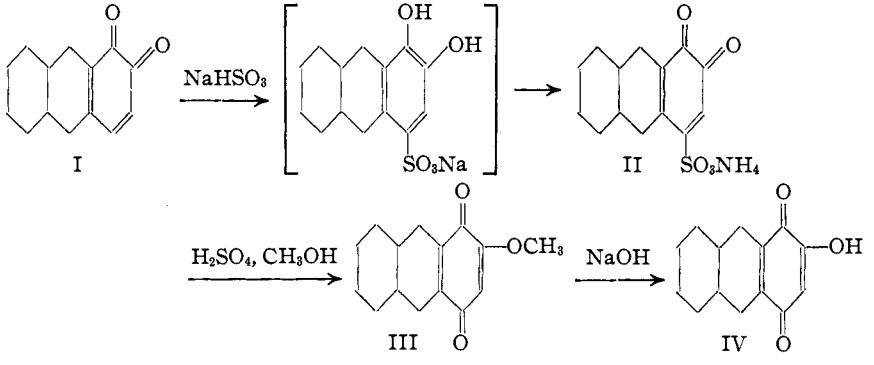
The interest attaching to the properties of hydroxynaphthoquinone, in particular with regard to the abnormal course of its alkylation reactions[1] and the position of the equilibrium between its tautomeric forms,[2] renders it a matter of some importance to examine the hitherto unknown compound named in the title. The chemistry of anthracene is so different from that of naphthalene that it should be possible to determine, in this way, if the phenomena referred to are at all general.

The most satisfactory method found for the preparation of 2-hydroxy-1,4-anthraquinone is indicated as follows



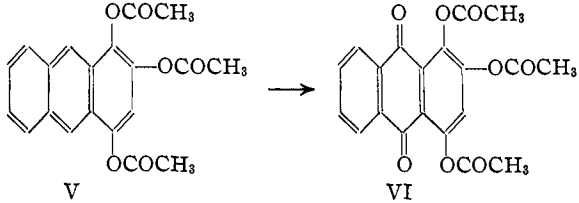
The conversion of II into III involves hydrolysis of the sulfonate group, tautomeric change to IV, and esterification. Good yields were obtained in all of the reactions when pure materials were employed, but it was found most convenient to use crude 1,2-anthraquinone,[3] when the over-all yield from β-anthrol was only 23% of the theoretical. The sulfonate, II, was also obtained from 1-nitroso-2-anthrol.[3] This was converted, by acidifying its solution in sodium bisulfite solution, into 1-amino-2-anthrol-4-sulfonic acid, and the latter was easily oxidized to the quinone, II, by nitric acid. The yield, however, was very poor.

[1] (a) Fieser, THIS JOURNAL, **48**, 2922 (1926); (b) **48**, 3201 (1926); (c) **49**, 857 (1927).

[2] Fieser, *ibid.*, **50**, 439 (1928).

[3] Lagodzinski, *Ann.*, **342**, 59 (1905).

The structure of this hydroxyanthraquinone was established by oxidizing its hydroquinone triacetate, 1,2,4-triacetoxy-anthracene (V), with chromic

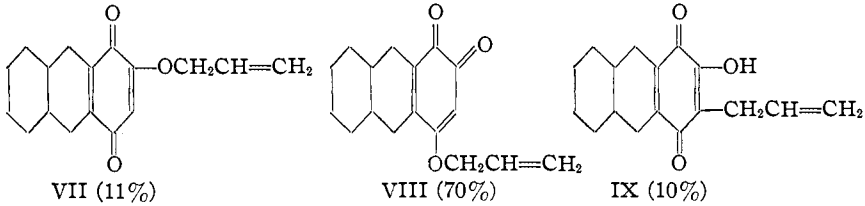


V VI

acid. The resulting substance was found to be identical with a sample of triacetylpurpurin, VI, prepared from purpurin.

2-Hydroxy-1,4-anthraquinone resembles the corresponding naphthoquinone to a marked degree. The only noteworthy difference between the two substances is that the former does not form a bisulfite addition product and, therefore, unquestionably has the *p*-quinonoid structure. The compound, which crystallizes in yellow needles, displaces even acetic acid from solutions of its salts, it reacts readily with amines and it is esterified by methyl alcohol in the presence of mineral acids to give II. This ether, together with 4-methoxy-1,2-anthraquinone, is produced in the ratio of 33% of the former to 62.5% of the latter by the action of methyl iodide on the silver salt of 2-hydroxy-1-4-anthraquinone. The isomers exhibit all of the properties characteristic of the corresponding methoxynaphthoquinones;[1a] the *o*-quinone ether, for example, forms a soluble bisulfite compound and is converted into the isomer by the action of methyl alcohol and hydrogen chloride.

Allyl bromide reacts with the silver salt of 2-hydroxy-1,4-anthraquinone with the formation of three isomers in the proportions indicated.



VII (11%) VIII (70%) IX (10%)

According to views previously expressed,[1a,b] VII is the result of simple methathesis, VIII is produced as a result of the 1,4-addition of the alkyl halide, while IX, which can also be prepared by the rearrangement of VIII, here results from the 1,2-addition of the alkyl halide. The relative yields of the isomers are very nearly the same as in the allylation of hydroxynaphthoquinone, and this is also true of the results of methylation.

All of these facts indicate that the presence of the additional benzene ring is of little consequence; the dominant feature in the structures of these hydroxy quinones of the naphthalene and anthracene series is the

grouping, O=C—CH=C—OH, which, as Claisen first observed,[4] is almost equivalent to a carboxyl group.

The normal reduction potentials of some of the quinones here described are given in Table I. The determinations were carried out by electrometric titration of the quinone with titanous chloride or of the catalytically prepared hydroquinone solution with an oxidizing agent according to a procedure previously described.[2] Solvent "C" was employed in the cases noted because, being essentially neutral, it does not cause hydrolysis of the *o*-quinone ether. ΔE_1 and ΔE_2 indicate the slope of the titration curve; the theoretical value is 17.8 mv.

TABLE I

REDUCTION POTENTIALS AT 25°

Solvents: A, 0.1 *N* HCl; B, 50% alcohol, 0.1 *N* in HCl and 0.2 *N* in LiCl; C, 37% alcohol, 0.047 *M* in KH_2PO_4 and 0.047 *M* in Na_2HPO_4.

Compound	Solvent	Titrated with	E_0, v.			ΔE_1, mv.	ΔE_2, mv.	E_0 (av.)
2-Hydroxy-1,4-anthraquinone	B	$TiCl_3$	0.275	0.275		18.5	18.2	0.275
2-Methoxy-1,4-anthraquinone	C	$K_4Fe(CN)_6$	.272	.273		19.0	19.4	.272
4-Methoxy-1,2-anthraquinone	C	$K_4Fe(CN)_6$	.347	.345	0.346	18.8	19.5	.346
1-Methyl-5,6-(β,β-naphtho)-3,4-coumarane-quinone	B	$TiCl_3$	.304	.306	.304	18.1	17.9	.305
1,2-Anthraquinone-4-sulfonic acid	A	$TiCl_3$	.530	.530		18.6	18.2	.530
1,2-Anthraquinone	..	.....	....	....	....	....	....	.490[5]
1,4-Anthraquinone[6]	B	$TiCl_3$	.401	.404	.399	17.4	17.8	.401

In Table II is given a comparison of these values with the normal potentials under similar conditions of the corresponding naphthoquinones.

TABLE II

DIFFERENCE IN POTENTIAL BETWEEN α- AND β-NAPHTHOQUINONES AND α- AND β-ANTHRAQUINONES IN MILLIVOLTS

Substituent	None	OH	OCH_3	SO_3H	$—CH_2CH(CH_3)O—$
α-Quinones	82	81	81	...	...
β-Quinones	89	..	87	98	101

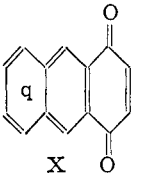
The α- and β-anthraquinones are lower in potential than the similarly constituted naphthoquinones by from 81 to 101 mv., which, considering that seven pairs of compounds of different types are compared under a variety of solvent conditions, represents a fairly constant quantity and is suggestive of some fundamental relationship.

[4] Claisen, *Ann.*, **281**, 306 (1894); **291**, 35 (1896); *Ber.*, **59**, 152 (1926).

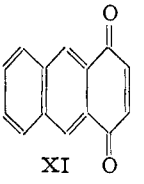
[5] Conant and Fieser, THIS JOURNAL, **46**, 1858 (1924), determined this value for 95% alcohol 0.5 *N* in HCl.

[6] The sample was prepared according to Dienel, *Ber.*, **39**, 931 (1906).

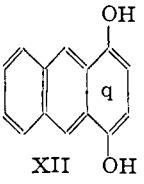
If the para-bond structure is disregarded, there are two possible formulas for a compound such as 1,4-anthraquinone. Formula X does not explain



X



XI



XII

the observed relationship because it contains an *o*-quinonoid nucleus which should render the substance more, rather than less, reactive than α-naphthoquinone, in which a stable benzene ring is fused to the *p*-quinone group. It is not easy to judge of the properties of a compound possessing the structure of XI, but it does not seem at all likely that the substance would be any less reactive than α-naphthoquinone. Thus it does not appear that the difference in the potentials of these bi- and tricyclic quinones is connected with the structures of these quinones and an explanation must be sought by considering the structures of the reduction products.

In terms of the *o*-quinonoid theory of the structure of anthracene, XII should possess an added reactivity as a result of its *o*-quinonoid nucleus and it should be, in this respect, comparable with 9,10-anthrahydroquinone. This would mean that the corresponding quinone should have a lower reduction potential than quinones which are similar to it but which do not pass into anthracene derivatives on reduction, and this is, indeed, the case. The low reduction potential of 9,10-anthraquinone has been attributed to this same factor[7] and it is interesting to see how the potentials of the two *p*-quinones of the anthracene series compare. 9,10-Anthraquinone differs from 1,4-anthraquinone essentially in that both of its quinonoid linkages are members of benzene rings, while with the isomer only one linkage is so involved. The same relationship exists between α-naphthoquinone and *p*-benzoquinone, and the difference in their potentials is 0.224 v. It would be expected, then, if the quinone structures are of relatively little significance, that 1,4- and 9,10-anthraquinone would differ in potential by about this same amount, and the actual difference, 0.246 v., is not far from this value. This seems to establish the correctness of the interpretation adopted, namely, that 1,4-anthraquinone is comparable with 1,4-naphthoquinone and that its reduction product is comparable with 9,10-anthrahydroquinone. The *o*-quinonoid formula, X, hardly expresses the similarity to α-naphthoquinone, while, if Formula XI is adopted, it must be considered that the compound has at least no very pronounced added reactivity as a result of the tetraketone structure.

Regarding the question of the possible tautomerism of 2-hydroxy-1,4-

[7] Fieser and Ames, THIS JOURNAL, **49**, 2604 (1927).

anthraquinone, the chemical properties of the substance clearly show that the less stable β-anthraquinone form must be present in only a very small concentration in the equilibrium mixture, though it is necessary to consider that this form is capable of at least transitory existence. Assuming that the difference in potential of the two tautomers is equal to the difference in the potentials of the corresponding ethers, the constant of the tautomeric equilibrium may be calculated with the use of the equation previously developed.[2] It is found that $K = 316$, which means that 99.7% of the substance is present at equilibrium in the α-anthraquinone form. It is clear that the chemical and electrochemical evidence are in good agreement with each other, and that in this respect, also, the bi- and tricyclic quinones are very similar.

Experimental Part

1,2-Anthraquinone-4-sulfonic Acid.—A slight modification of the usual procedure[8] for the reduction of sodium anthraquinone-β-sulfonate greatly shortened the time required for the operation. A mixture of 150 g. of this salt,[9] 90 g. of zinc dust, 800 cc. of ammonia solution (sp. gr. 0.90) and 350 cc. of water was placed in a flask equipped with a reflux condenser and a mechanical stirrer. The mixture was warmed on the water-bath to such a temperature that only slight frothing occurred, the temperature being increased as reduction proceeded. After about four hours reduction was complete and the precipitated product was separated from the brown filtrate while the latter was still hot. By suspending the precipitate in 3 liters of water and allowing the zinc to settle to the bottom, the greater part of the metal could be separated mechanically and the sodium anthracene-β-sulfonate obtained was suitable for conversion into β-anthrol. For this purpose the anthracene sulfonate from 200 g. of the quinone was fused with 900 g. of potassium hydroxide according to the directions of Lagodzinski;[3] yield, 80–90 g.

The 1,2-anthraquinone[10] prepared in the manner described by Lagodzinski was found to contain considerable inert material which is not easily removed on a large scale, but which does not greatly interfere with the reaction of the quinone with sodium bisulfite. The quinone obtained from 60 g. of β-anthrol, while still moist, was made into a paste with 500 cc. of water, 35 g. of sodium bisulfite was added and the mixture was stirred mechanically for two hours. The quinone rapidly dissolved while a fine

[8] Liebermann, *Ann.*, **212**, 57 (1882).

[9] I am indebted to the E. I. du Pont de Nemours & Co. for a large supply of this material.

[10] Attempts to convert this quinone into a dihydroxy derivative by the action of calcium oxychloride, following the methods employed for the preparation of isonaphthazarin, were unsuccessful. In no case was there any evidence of the formation of such a quinone; the sole product isolated, separated from considerable black material by extraction with dilute hydrochloric acid, was a colorless acid, very readily soluble in water and melting at 232°. It is probably the lactone acid, $C_{10}H_6\begin{matrix}CO\\ \diagup\quad\diagdown O\\ CHCHOHCOOH\end{matrix}$, corresponding to the oxidation product of β-naphthoquinone obtained by Zincke, *Ber.*, **25**, 405 (1892).

Anal. Calcd. for $C_{14}H_{10}O_5$: C, 65.11; H, 3.91. Found: C, 65.33; H, 3.80.

suspension of black material remained unaltered. The mixture was then warmed to the boiling point and a solution of 25 cc. of sulfuric acid in 80 cc. of water was slowly added. A few drops of caprylic alcohol served to prevent foaming due to the evolution of sulfur dioxide. The hot solution was filtered through a large folded paper and to the dark brown filtrate, after cooling to room temperature, was added a solution of 21 g. of chromic acid in a small volume of water. The solution became deep red in color and, after adding 200 cc. of saturated sodium chloride solution, the sodium salt of 1,2-anthraquinone-4-sulfonic acid separated in the form of a fine, crystalline powder. It was washed with dilute sodium chloride solution and dried at 120°; yield, 50 g. (52%, based on the weight of β-anthrol). When pure 1,2-anthraquinone was employed for this reaction instead of the crude material, the yield of the sulfonate, which was isolated in the form of the ammonium salt in the manner described below, was 74% of the theoretical quantity.

The sodium salt is readily soluble in water and crystallizes in the form of small, dark red needles.

Anal.[11] Calcd. for $C_{14}H_7O_5SNa$: Na, 7.41. Found: 7.27.

Neutral solutions of this compound do not undergo decomposition as readily as is the case with β-naphthoquinone sulfonate, but the substance is rapidly converted into brown products in the presence of alkali. The quinone forms a colorless bisulfite addition product and readily reacts with aromatic amines to give red, alkali-soluble anilino-quinones.

The ammonium salt was obtained by adding an excess of saturated ammonium nitrate solution to a solution of the sodium salt in hot water. The two salts are easily distinguished, for, when each is precipitated by salting out, the sodium derivative separates in the form of a bright red suspension which is very difficult to filter and dry, while the ammonium salt forms a compact, dull red precipitate. The conversion is nearly quantitative when the sodium salt employed is pure; the crude material described above apparently contained considerable sodium chloride for it yielded only 58% of the theoretical quantity of the ammonium salt. The ammonium sulfonate dissolves readily in alcohol or water but the solutions rapidly undergo decomposition. Crystallized from a dilute ammonium nitrate solution, it formed small, dark red prisms.

Anal.[11] Calcd. for $C_{14}H_{11}O_5NS$: S, 10.50. Found: 10.14.

The β-anthraquinone sulfonate was also obtained from nitroso-β-anthrol, though the process was less satisfactory than that given above. The nitroso compound, in the form of its sodium salt, was treated with a solution of sodium bisulfite (2 molecular equivalents), the solution was filtered from a rather considerable quantity of black material, and a large excess of sulfuric acid was added. After standing at 30–40° for one week, the separation of yellow crystals of **1-amino-2-anthrol-4-sulfonic acid** had ceased, the yield being 10–15% of the theoretical. The low yield is probably due both to a partial destruction of the nitroso compound by the bisulfite and to incomplete reduction of the intermediate product by sulfur dioxide. The sulfonic acid derivative, which is insoluble in water, crystallized from 10% bisulfite solution in the form of yellow needles containing combined water which was not eliminated on drying *in vacuo* at 100°.

Anal.[11] Calcd. for $C_{14}H_{11}O_4NS.{}^1/_2H_2O$: S, 10.75. Found: 10.49.

On stirring this compound into 25% nitric acid, oxidation rapidly took place and crystallization of ammonium 1,2-anthraquinone-4-sulfonate occurred.

2-Hydroxy-1,4-anthraquinone.—To a suspension of 10 g. of β-anthraquinone ammonium sulfonate in 100 cc. of methyl alcohol, 15 cc. of concd. sulfuric acid was

[11] Analysis of Dr. F. H. Case.

slowly added while the mixture was well shaken. The salt rapidly dissolved, the solution warmed and became deep red in color, sulfur dioxide was given off and suddenly a yellow substance separated and the flask was soon filled with a thick, crystalline paste. After allowing the mixture to cool, the product was collected and washed well with methyl alcohol. Addition of water to the filtrate causes the precipitation of only a negligible quantity of impure material. The yellow product, 2-methoxy-1,4-anthraquinone (see below), was nearly pure; yield, 6.6 g. (85%). It was boiled with 600 cc. of water and 5 cc. of 6 *N* sodium hydroxide solution until most of the material had dissolved, the orange-yellow solution was filtered and the residue boiled with sufficient dilute alkali to dissolve it. The sodium salt of hydroxyanthraquinone was precipitated by adding 15 cc. of 6 *N* alkali to the combined filtrates. It separated from the solution while still hot in the form of a red powder. On acidifying the solution of this salt in boiling water, 2-hydroxy-1,4-anthraquinone separated in the form of very slender, bright yellow needles, and in very pure condition; yield, 5.7 g. (92%).

2-Hydroxy-1,4-anthraquinone is moderately soluble in glacial acetic acid or in alcohol, sparingly soluble in benzene, ether or water, and dissolves only to a very slight extent in bisulfite solution. The solution in concd. sulfuric acid is claret red, the sodium hydroxide, carbonate or acetate solution is pale orange-yellow, while the vat is orange-red. The substance condenses with aromatic amines in glacial acetic acid solution to give alkali-insoluble anilino-quinones. It crystallizes from toluene or glacial acetic acid in the form of yellow needles which melt with decomposition at 243°, a red color being imparted to the glass capillary even above the point of fusion.

Anal. Calcd. for $C_{14}H_8O_3$: C, 74.99; H, 3.60. Found: C, 74.81; H, 3.76.

The sodium salt, prepared as described above and crystallized from water, formed orange micro-needles which dissolve readily in water but which are very sparingly soluble in dilute sodium hydroxide solution.

Anal. Calcd. for $C_{14}H_7O_3Na$: Na, 9.35. Found: 9.36.

The silver salt was prepared by precipitation from a solution of the ammonium salt at 60°; the material was at first gelatinous but in a few seconds it changes into a crystalline, dark red powder.

Anal. Calcd. for $C_{14}H_7O_3Ag$: Ag, 32.59. Found: 32.42.

The acetyl derivative was obtained by the action of acetic anhydride and a small quantity of concd. sulfuric acid on the quinone. Crystallized from alcohol, in which it is sparingly soluble, or from benzene, which readily dissolves the material, it forms yellow plates melting at 195°.

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.17; H, 3.79. Found: C, 72.02; H, 3.86.

1,2,4-Triacetoxy-anthracene was prepared by boiling for ten minutes a mixture of 2 g. of the hydroxyanthraquinone, 5 g. of sodium acetate, 6 g. of zinc dust and 40 cc. of acetic anhydride. The solution was filtered while hot, the residue washed with hot glacial acetic acid and water was added to the hot filtrate. The acetyl derivative separated in crystalline form and in nearly quantitative yield. It is moderately soluble in benzene or glacial acetic acid, and the solutions, particularly when dilute and when viewed in thin layers, exhibit pronounced blue fluorescence. It is best crystallized from benzene-ligroin, forming colorless needles; m. p. 191°.

Anal. Calcd. for $C_{20}H_{16}O_6$: C, 68.16; H, 4.58. Found: C, 68.06; H, 4.62.

On boiling a solution of 1 g. of this anthracene derivative in glacial acetic acid with 0.8 g. of chromic acid for five minutes, adding a little water and cooling, **triacetyl purpurin** was obtained. After repeated crystallization from alcohol, the melting point of the yellow needles remained constant at 202–203°, and no depression of the melting

point was produced on admixture of a sample of the triacetyl derivative (m. p. 202–203°) prepared from purpurin. Schunck and Roemer[12] report a melting point of 198–200°.

Anal. Calcd. for $C_{20}H_{14}O_8$: C, 62.82; H, 3.69. Found: C, 62.75; H, 3.85.

Methylation

A mixture of 4 g. of 2-hydroxy-1,4-anthraquinone silver salt, 2 g. of methyl iodide and 40 cc. of benzene was shaken mechanically until the red salt had disappeared (about ten hours), and the product was then extracted with benzene and the solvent evaporated under diminished pressure. The finely-powdered material was first triturated with ammonia solution to remove a small quantity (0.14 g.) of the hydroxy compound and then with successive portions of bisulfite solution to remove the *o*-quinone isomer formed. This was precipitated from the solution by the addition of sodium carbonate; yield, 1.71 g. (62.5% of the theoretical amount, allowing for the hydroxy compound recovered); m. p., 197°. The residue insoluble in bisulfite solution was the somewhat impure *p*-quinone ether; yield, 0.9 g. (33%).

4-Methoxy-1,2-anthraquinone.—Crystallized from benzene, in which it is moderately soluble, the compound formed clusters of fine, yellow needles melting at 198°.

Anal. Calcd. for $C_{15}H_{10}O_3$: C, 75.61; H, 4.23. Found: C, 75.52; H, 4.48.

The ether dissolves readily in bisulfite solution, gives a claret-red solution in concd. sulfuric acid, and is readily hydrolyzed by boiling with dilute alcoholic hydrochloric acid or with alkali. On boiling for a short time a solution of the substance in methyl alcohol containing a small quantity of concd. sulfuric acid it is completely converted into the isomeric *p*-quinone ether.

2-Methoxy-1,4-anthraquinone.—The material obtained directly from ammonium β-anthraquinone sulfonate is nearly pure but contains a trace of a dark-colored by-product which is best removed by crystallization from toluene with the use of animal charcoal. Small, yellow needles melting at 217° are thus obtained.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 75.61; H, 4.23. Found C, 75.54; H, 4.53.

This ether is moderately soluble in benzene, toluene or glacial acetic acid, insoluble in bisulfite solution, and it dissolves without change in concd. sulfuric acid with a claret-red color. It is not readily hydrolyzed by dilute alcoholic hydrochloric acid. The material prepared in the above manner was compared with samples obtained by esterifying hydroxyanthraquinone with methyl alcohol and hydrogen chloride and by methylation with methyl iodide. The substances were identical.

Allylation

Three products are formed in the reaction of hydroxyanthraquinone silver salt with allyl bromide and they may be readily separated by taking advantage of the solubility of the *o*-quinone ether in bisulfite solution and of the acidic nature of the C-alkyl derivative. A mixture of 8.9 g. of the silver salt, 150 cc. of benzene and 3.5 g. of allyl bromide was boiled for one-half hour and the silver bromide separated. Most of the *o*-quinone ether crystallized from the filtrate; the mother liquor, diluted with ether, was extracted with ammonia solution and then with bisulfite solution and the products were recovered in the usual way. From the mother liquor, dried and concentrated, the *p*-quinone ether was obtained by the addition of petroleum ether; it was somewhat dark in color but melted only a few degrees below the correct temperature. The other isomers were nearly pure. Yields: *o*-quinone ether, 4.9 g. (70%); *p*-quinone ether, 0.8 g. (11%); C-alkyl derivative, 0.7 g. (10%).

[12] Schunck and Roemer, *Ber.*, 10, 553 (1877).

4-Alloxy-1,2-anthraquinone.—This compound is best crystallized from benzene, in which it dissolves readily; it separates in the form of flat, yellow needles; m. p. 173°. It readily undergoes rearrangement, as indicated below.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.22; H, 4.78.

2-Alloxy-1,4-anthraquinone.—In order to remove dark-colored by-products it was necessary to precipitate the crude material several times from its solution in glacial acetic acid by the addition of water; the ether was then crystallized repeatedly from benzene-ligroin and obtained in the form of light yellow blades melting at 139°.

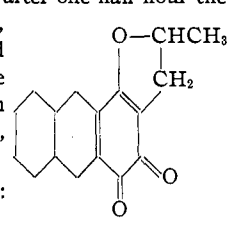
Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.28; H, 4.67.

2-Allyl-3-hydroxy-1,4-anthraquinone.—This compound dissolves readily in glacial acetic acid and crystallizes from this solvent in the form of beautifully lustrous, flat, yellow needles melting at 215°. It is readily soluble in benzene, moderately soluble in alcohol, and the alkaline or alkali carbonate solution is orange in color.

Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 76.90; H, 4.68.

The same substance is easily obtained by the rearrangement of 4-alloxy-1,2-anthraquinone. Three and one-half g. of the ether was heated in an oil-bath maintained at 175°. As soon as fusion was complete the temperature of the melt rose rapidly to 220° and the vessel was at once removed from the oil-bath. The melt quickly solidified and now failed to fuse at 175°. The product was extracted with ammonia solution and crystallized once from alcohol; yield, 3 g.; m. p. 214°.

1-Methyl-5,6-(β,β-naphtho)-3,4-coumaranquinone.—One g. of allylhydroxyanthraquinone was dissolved in 7 cc. of concd. sulfuric acid and after one-half hour the claret-red solution was poured into water. The somewhat oily, red precipitate was dissolved in bisulfite solution and recovered by acidification of the solution, when it separated in crystalline condition. After several crystallizations from benzene-ligroin the melting point remained constant at 186–187°, and small, orange-red needles were obtained.



Anal. Calcd. for $C_{17}H_{12}O_3$: C, 77.25; H, 4.58. Found: C, 77.01; H, 4.85.

This coumaran derivative is attacked only very slowly by dilute alkali in the cold but on warming it is rapidly dissolved, giving an orange-red solution from which acids precipitate a yellow substance in crystalline condition. The compound crystallizes from benzene, in which it is only moderately soluble, in the form of small, yellow needles, m. p. 211–212°. The acidic character and the color of the material, together with the analysis, indicate the structure of **2-(β-hydroxypropyl)-3-hydroxy-1,4-anthraquinone.**

Anal. Calcd. for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00. Found: C, 72.05; H, 5.34.

Summary

2-Hydroxy-1,4-anthraquinone has been prepared and its structure established by conversion into triacetylpurpurin. The silver salt of this quinone reacts with a saturated alkyl halide to give a mixture of the products of metathesis and of 1,4-addition, while with allyl bromide a C-alkyl derivative, the product of 1,2-addition, is also formed. These and other results show that the properties and reactions of 2-hydroxy-1,4-anthraquinone are strikingly similar to those of 2-hydroxy-1,4-naphthoquinone.

The reduction potentials of α- and β-anthraquinones are from 81 to

101 mv. lower than those of the corresponding naphthoquinones, while α-anthraquinone is 246 mv. higher in potential than 9,10-anthraquinone. These facts are consistent with the conception that α-anthraquinone is in every way comparable to α-naphthoquinone, but that its reduction product should be compared with 9,10-anthrahydroquinone.

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THE ISOMERISM OF PHENYLPHTHALIMIDE AND A STUDY OF THE NITRO AND CHLORO DERIVATIVES

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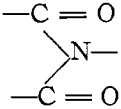
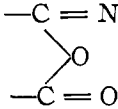
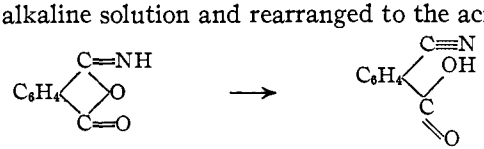
A critical study of the extensive work which has been done on phenylphthalimide or phthalanil, and its derivatives shows not only conflicting theoretical interpretations but contradictory experimental results. In addition to the closely related compounds the phthalanils, the phthalanilic acids, and the phthalamides which have not always been completely separated from one another, there are the two isomeric phthalimides—the symmetrical type —C = O and the asymmetrical type —C = N—.





These isomers differ so slightly in their physical and chemical properties that the separation and identification have been difficult and this accounts for much of the confusion and inaccuracy in the reported results. In the present study a complete survey of the literature was made and much of the experimental work repeated, duplicated in some cases and in the case of disputed points additional evidence has been obtained. The more general methods of preparation of the phthalanils and the phthalanilic acids have not been a matter of controversy, but this is not true of the preparation and isolation of the isomeric phthalanil derivatives.

The first evidence of the existence of an isomeric phthalimide was reported by Hoogewerff and van Dorp.[1] They found that *o*-cyanobenzoic acid was obtained by the action of ammonia on phthalyl chloride. Since neither phthalimide nor the phthaldiamide can be transformed by ammonia into the *o*-cyanobenzoic acid, they assumed the formation of an asymmetrical phthalimide as an intermediate compound—this evidently was unstable in alkaline solution and rearranged to the acid, thus



[1] Hoogewerff and van Dorp, *Rec. trav. chim.*, 11, 84 (1892).