that previously noted with RMgX compounds like benzylmagnesium chloride which give nuclear disubstituted products with a more restricted class of reactants. A mechanism, based on intermediate free radicals, has been suggested for the cinnamyl transformations.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

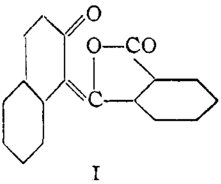
THE CONDENSATION OF BETA-NAPHTHOL WITH PHTHALIC ANHYDRIDE

BY LOUIS F. FIESER

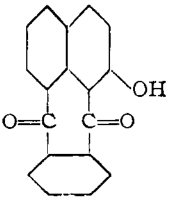
RECEIVED JULY 28, 1931 PUBLISHED SEPTEMBER 5, 1931

The appearance of a paper by Rieche and Frühwald[1] on a compound described as "phthaloyl-β-naphthol" prompts me to publish at this time results obtained in an investigation of the same subject, even though this work is not yet completed. The results to be presented offer certain obstacles to an acceptance of the structural formula proposed by the German investigators, and my work thus leads to a different conception of the nature of the interesting compound which results in excellent yield from the condensation of the reactants noted.

The present work originated in the discovery by Emma M. Dietz in the Bryn Mawr laboratory that the process described in the patent literature[2] for the condensation of β-naphthol with phthalic anhydride in the presence of aluminum chloride does not lead to the formation of an hydroxynaphthanthraquinone as claimed in the patent, but to a yellow substance, $C_{18}H_{10}O_3$, having quite different properties.[3] As a possible structure, she proposed formula I, which was suggested by the structure assigned by Schaarschmidt[4] to a somewhat similar condensation product from α-anthrol, although the evidence for his structure was very incomplete. In continuing her brief study, it was soon found that formula I is ruled out by the fact that the yellow substance has one active hydrogen atom.



I



II

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[1] Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

[2] Fr. Bayer and Co., German Patent 298,345 (1916); Friedländer, *Fortschritte der Teerfarbenfabrikation*, **13**, 390 (1923–1924).

[3] Dietz, Dissertation, Bryn Mawr, 1929.

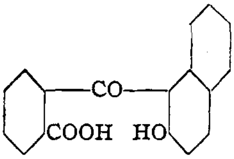
[4] Schaarschmidt, *Ber.*, **49**, 381 (1916).

As Rieche and Frühwald have observed, the compound forms a colorless acetate.

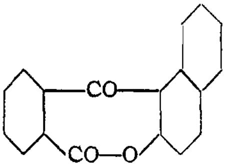
The only other reaction reported on by the German investigators is the alkali fusion. Under certain conditions they were able to obtain 7-hydroxynaphthalene-1-carboxylic acid as a degradation product, and on the basis of this fact they have proposed for the compound the structure of II. It is not inconsistent with this formula that the substance forms a monoethyl derivative with diethyl sulfate, or that phosphorus pentachloride replaces an hydroxyl group by chlorine, as detailed in the experimental portion of this paper. On the other hand, while the formula indicates the presence of one active hydrogen atom and two carbonyl groups, a quantitative test with the Grignard reagent revealed the presence of only one carbonyl group in addition to the one active hydrogen atom. With a large excess of phenylmagnesium bromide in boiling benzene, the yellow substance is converted only into a monophenyl derivative. This forms a colorless diacetate. The action of the Grignard reagent is not easily accounted for by the formula under discussion, and no improvement in the position is made by assuming a tautomeric shift of the hydroxylic hydrogen to the neighboring carbonyl group.

A further observation which is out of harmony with formula II is that the substance appears to have the properties of a lactone. It dissolves only slowly in boiling alkali, and analyses of the dried barium and sodium salts indicate that they are formed not by the replacement of hydrogen by a metal but by the addition of the elements of the metal hydroxide.

In attacking the problem further, studies have been made of the synthesis of the compound and of the oxidative degradation. If the reaction of β-naphthol with phthalic anhydride followed the normal course, it would yield 2-(2′-hydroxynaphthoyl-1′)-benzoic acid, III, rather than the abnormal product. Since the latter substance is best produced at a high temperature (250°), it seemed possible that the reaction might proceed through the primary formation of the acid which would be expected to result from the normal condensation. Rieche and Jungholt[5] recently have shown that earlier workers erroneously assigned formula III to an entirely different compound, and that the acid was still unknown. I had no success in attempting to prepare it by reacting β-naphthol with



III



IV

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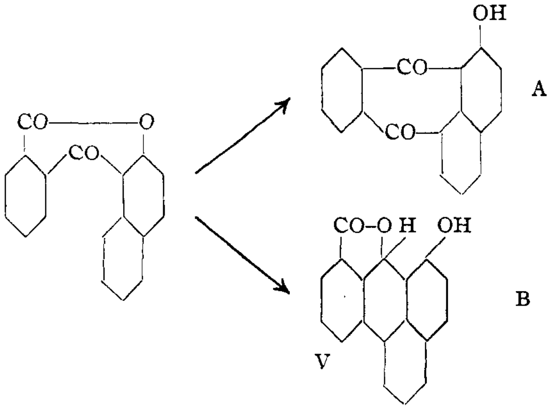
[5] Rieche and Jungholt, *Ber.*, **64**, 578 (1931).

phthalic anhydride at a low temperature, but found that it may be obtained with ease through the use of β-naphthol methyl ether. In tetrachloroethane solution, the chief product of reaction at room temperature was a methyl ether, which yields the acid, III, on demethylation with aluminum chloride; at the temperature of the steam-bath, this acid itself was produced. It is easily isolated in the form of the nicely crystalline lactone, IV.

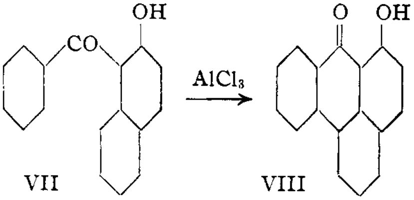
The ready formation of a lactone indicates that the phthalic acid residue has entered either the 1- or the 3-position of β-naphthol, and a choice between the two possible formulas is furnished by the fact that the new acid does not couple. A slight coloration is produced by the addition of a diazonium salt to an alkaline solution of the acid, but there is no coloration whatsoever when the ester is used or in carrying out a similar test with the reduction product, 2-(2′-hydroxynaphthyl-1′)-benzoic acid. Since 3-substituted β-naphthols couple while the 1-substituted derivatives do not, the new acid obviously has the structure III.

The supposition that the new compound is an intermediate in the formation of the abnormal reaction product has proved to be correct. The acid itself forms only a salt when heated with aluminum chloride in benzene solution, but when the lactone, IV, is subjected to similar treatment, it is converted smoothly into the yellow product, with which it is isomeric. This ready isomerization is not easily accounted for. The formula proposed by Rieche and Frühwald would give an acceptable description of the reaction (Scheme A), were it not for the fact that the properties of the product do not correspond well with their formula. Another course for the reaction, and one which appeared more reasonable in the early stages of this investigation than it does now, is indicated by Scheme B. This represents the result of a Scholl peri-condensation to give a benzanthrone, reduction of the ketone group by the hydrogen liberated, and readjustment of the lactone ring to a more stable position. Formula V, to

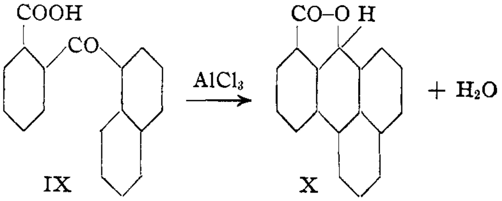


be sure, is consistent neither with the alkali fusion results of Rieche and Frühwald nor with the oxidative degradation to be described below; but it is worth mentioning on account of the fact that the actual compound in question reacts in accordance with the demands of a formula of this type. It has the properties of an aromatic γ-lactone; it has one hydroxyl group and only one carbonyl group.

A peri-condensation such as B, moreover, is not without parallel. Fierz-David and Jaccard[6] state that 1-benzoyl-2-naphthol may be condensed to 4-hydroxybenzanthrone, VIII, and a confirmation of this statement is given later in this paper. It may be noted that this compound is only sparingly soluble in alkali and that it is ethylated only with difficulty. Similar properties have been noted for the abnormal condensation product under consideration. A closer analogy, though one which is based upon less sound evidence, is found in the intramolecular condensation of α-naphthoyl-*o*-benzoic acid, IX, by heating with sodium aluminum chloride, as described in a recent patent.[7] The substance produced is said to have the structure of X. Following the patent specifications with some modifications, a substance having the composition of X has been obtained. It is a colorless, stable substance which is insoluble in alkali but which with alcoholic alkali yields a salt from which the original compound is regenerated on acidification. The substance thus has the properties of a lactone. As far as the present information goes, the compound may have the structure suggested, and this seems to show that a condensation in the manner of Scheme B, above, is possible.



VII VIII



IX X

While from a consideration confined to the properties of the abnormal yellow compound, and to the method by which it is formed, formula V appears to give a reasonable account of the facts, it is of course out of harmony with the results of the alkali fusion, in so far as these results have

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[6] Fierz-David and Jaccard, *Helv. Chim. Acta*, **11**, 1042 (1928).

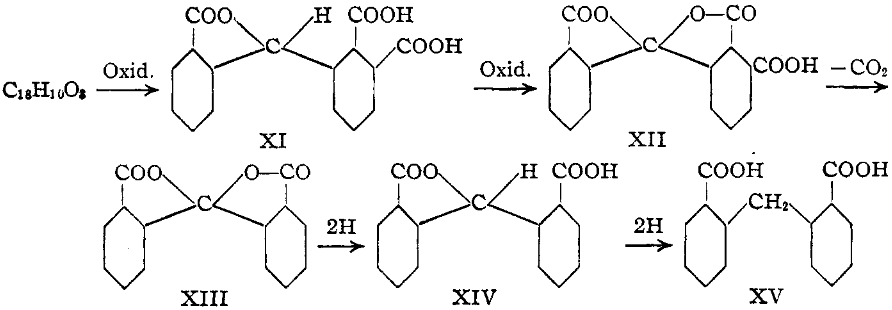
[7] I. G. Farbenind., English Patent 303,375 (1930).

been reported. Rieche and Frühwald make the preliminary statement that under certain conditions the alkali fusion yields a product which may be an hydroxybenzanthrone; if this observation is confirmed it may well be in just as good accord with formula V as with their structure, II. On the other hand, the oxidation experiments which will now be described are difficult to reconcile with either formula.

The yellow oxidation product is attacked readily by potassium permanganate in alkaline solution and it rapidly takes up the equivalent of seven atoms of oxygen. There is a pause in the oxidation at this point and from the mixture there is easily isolated in good yield a colorless dibasic acid which readily forms an anhydride. On more vigorous treatment with alkaline permanganate this dibasic acid loses two atoms of hydrogen with the formation of a monobasic acid. One of the carboxyl groups of the dibasic acid must be present in the second oxidation product in masked form, that is, as a part of a lactone ring. The second oxidation product then must have produced an hydroxyl group at a point close to this acid group, and the reaction may be represented thus:

$$\left\{\begin{array}{l}\mathrm{COOH}\\ \mathrm{CH}\end{array}\right. \longrightarrow \left\{\begin{array}{l}\mathrm{COOH}\\ \mathrm{COH}\end{array}\right. \longrightarrow \left\{\begin{array}{l}\mathrm{COO}\\ \mathrm{C}\text{—}\end{array}\right.$$

The monobasic acid readily loses carbon dioxide and passes thereby into a known compound, the dilactone of benzophenone-2,2′-dicarboxylic acid (XIII, below). This substance has been described by Graebe and Juillard,[8] and the product here obtained, as well as the dimethyl ester of the free acid formed on careful hydrolysis, corresponds with the description given. The decarboxy compound, to be sure, was not identified at this point, but only after it had been reduced with zinc and alkali to the lactone of benzhydrol-2,2′-dicarboxylic acid, XIV, and further reduced by the action of fused potassium hydroxide to diphenylmethane-2,2′-dicarboxylic acid XV. These two reduction products and their derivatives also have been described by Graebe and Juillard, though they were prepared by somewhat different methods. The properties of the com-



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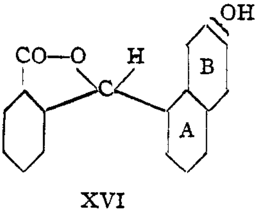
[8] Graebe and Juillard, *Ann.*, **242**, 214 (1887).

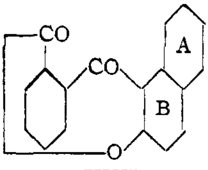
pounds here obtained agreed well with the descriptions given by these authors, and the lactone acid, XIV, was compared directly with a sample prepared according to the known methods.

It is not difficult to derive from these results the structure of the dibasic acid which results on oxidation of the yellow condensation product. In the reduction of XIII to XIV a lactone ring is opened by the alkali used and an alcoholic hydroxyl group is replaced by hydrogen. The result is that a carboxyl group has been set free and that the product differs from the starting material by two hydrogen atoms. It will be evident that this process represents the reversal of the oxidation of the primary oxidation product, the dibasic acid, to give a monobasic acid. This change, then, may be represented as in formulas XI and XII. The only question which remains is that of placing the carboxyl group which is present in the free form in both of these acids, and which is eliminated in the conversion of XII into the dilactone, XIII. A solution of this problem is furnished by the fact that the dibasic acid readily forms an anhydride. Were this substance alone considered, there would be two possible locations for the carboxyl group: either in the ring carrying the first acid group, and ortho to it, or attached to the central methane carbon atom. The second possibility is ruled out by the formation of the monobasic acid, XII, on oxidation. Therefore, the primary oxidation product is the lactone of benzhydrol-2,3,2′-tricarboxylic acid, XI.

The formation of the acid, XII, from the yellow condensation product represents the elimination of two carbon atoms. It may be inferred that these carbon atoms together with those of the two carboxyl groups in the oxidation product made up a benzene ring in the original compound. It is also evident that the hydroxyl group of the condensation product must be placed in this same ring. This leads to the view that the yellow substance has the outline skeleton of XVI. The analysis of the compound, however, shows that two hydrogen atoms must be abstracted from this formula. This must be done in such a way as to leave undisturbed the free positions of the phthalic anhydride residue and of Ring A. A formula such as V, above, thus appears to be out of the question.

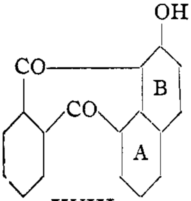


XVI

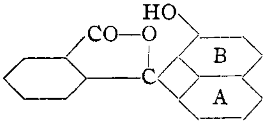


XVII

The results of degradation and of synthesis at first sight appear to lead to contradictory conclusions. According to the oxidation experiments the phthalic acid residue is joined to the ring in the naphthalene residue which does not carry the hydroxyl group, A in XVI. The ready conversion of the lactone of known structure, XVII, into the yellow isomer makes it seem highly probable that the phthalic acid part of the molecule is joined to B, the oxygen-carrying nucleus. There are, however, two ways of accounting for this apparent contradiction. One possible explanation is that one of the external carbon atoms of the phthalic anhydride part is joined to Ring A and that the second such atom is attached to Ring B. This is the situation in the structure proposed by Rieche and Frühwald and reproduced again in formula XVIII. It is easy to see how such a compound might be converted into the second oxidation product noted, XII; but the formation of the first such product, XI, is difficult to reconcile with this structure. Other objections to the formula have been noted above.

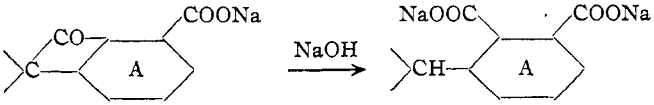


XVIII

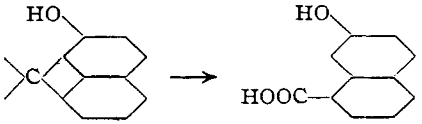


XIX

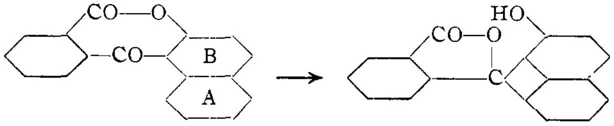
The only other possibility is that a single phthalic anhydride carbon atom is linked at the same time to Ring A and Ring B. This suggests the structure, XIX, which represents the substance as a peri-methylene compound having a cyclobutane ring. The lactone-like character of the substance, and the appearance of a lactone ring in the oxidation product, are well accounted for in this formula. It agrees with the number of functional groups detected by the Grignard reaction. According to this structure the alkaline oxidation would involve a rupture of the cyclobutane ring, and this might proceed through the formation of a cyclobutanone:



The alkali fusion would be interpreted as involving a rupture of the cyclobutane ring at the same point:



The cyclobutane formula will require further checking, but it is presented here as being in better accord with all of the facts known at the present time, than is any other structure suggested. The results of the study both of the synthesis and of the degradation of the abnormal reaction product indicate that the reaction can be formulated as an intramolecular phthalide condensation involving the addition of Ring A to the ketonic carbonyl group, followed by the rearrangement of a δ-lactone to a more stable γ-lactone ring:



I wish to thank Mr. Charles L. Bickel for carrying out the semi-micro analyses reported in this paper.

Experimental Part

1. Yellow Condensation Product, $C_{18}H_{10}O_3$ (XIX?)

The procedure described in the patent literature[2] gives fairly satisfactory results but it is greatly improved by increasing the quantity of phthalic anhydride and by altering somewhat the method of working up the product. One hundred grams of aluminum chloride was stirred into 320 g. of molten phthalic anhydride heated in an oil-bath maintained at 180°. Fifty grams of β-naphthol was then added and the bath was heated to 250° and kept there for one-half hour. The mixture should be stirred well and the material adhering to the walls of the flask may be melted down with a free flame. The thick, red-brown melt, while still hot, was poured with stirring into about 3 liters of hot water containing hydrochloric acid. In this way the product was easily disintegrated. The phthalic acid largely dissolved and the condensation product formed a light yellow, granular precipitate. This was collected, digested once with boiling, dilute hydrochloric acid, dissolved in boiling alkali, precipitated and digested once more with hydrochloric acid in order to remove traces of aluminum. There was thus obtained a nearly pure, light yellow product melting at 196–197°; yield, 92 g. (97%).

While this material was entirely satisfactory for some reactions (such as the oxidation), it still contained traces of aluminum. A completely pure product is easily obtained by distillation at diminished pressure, followed by crystallization from glacial acetic acid. The best samples were pure yellow and melted at 198° (R. and F., green-yellow, 196°). Analyses of this compound and of its acetate, m. p. 214°, confirmed the findings of Rieche and Frühwald.[1] An observation of these authors which I cannot confirm is to the effect that the yellow product is not altered by heating with zinc dust in alkaline solution. I have found that heating such a mixture overnight on the steam-bath is sufficient to convert the compound into a mixture which appears to contain at least two substances. Neither of these has as yet been isolated in pure form. A quantitative test in the modified Zerewitinoff apparatus was kindly carried out by Dr. E. M. Nygaard with the result that 1 mole of substance liberated 0.84 mole of gas and consumed a total of 1.82 moles of reagent.

Salts of the "yellow compound" were prepared by Miss Dietz. On boiling for a time with a solution of a metal hydroxide, the substance dissolves to give an orange-yellow solution from which the salt separates on cooling.

Anal. Calcd. for $C_{18}H_{11}O_4Na$: Na, 7.32. Found: 7.89. Calcd. for $C_{18}H_{11}O_4Ba^{1}/_{2}$: Ba, 19.09. Found: Ba, 18.81.

Ethyl Ether.—Attempts to alkylate the "yellow compound" with dimethyl sulfate were unsuccessful. With the more active diethyl sulfate a slow reaction took place so that by adding a large excess of reagent to an alkaline solution of the material heated on the steam-bath and stirred mechanically, a fair yield of the ether was eventually obtained. It dissolves easily in alcohol or benzene and forms stout yellow needles melting at 163°. It is insoluble in alkali.

Anal. Calcd. for $C_{20}H_{14}O_3$: C, 79.45; H, 4.67. Found: C, 79.52, 79.44; H, 4.73, 4.77.

Chloro Derivative.—A mixture of 5 g. each of the "yellow compound," phosphorus pentachloride and phosphorus oxychloride was stirred thoroughly and heated for fifteen minutes on the steam-bath. A vigorous reaction ensued, giving a clear solution. On pouring this into water, a good yellow precipitate was produced. This was extracted with glacial acetic acid from a small amount of colorless material and recovered from the solution by the addition of water. The product was then distilled and crystallized from alcohol, when it formed clusters of long yellow needles, m. p., 165°; yield, 4.3 g.

Anal. Calcd. for $C_{18}H_9O_2Cl$: C, 73.85; H, 3.10. Found: C, 73.97; H, 3.52.

The chloro compound slowly dissolves in boiling alkali and may be recovered from the solution unchanged. Attempts to replace the chlorine by hydrogen by heating with nitrobenzene, potassium acetate and copper powder led, rather, to the conversion of the substance into the original "yellow compound." The same substance was produced by the action of potassium permanganate on a solution of the chloro compound in a mixture of pyridine and alkali.

Phenyl Derivative.—The Grignard reaction was carried out by adding the phenylmagnesium bromide solution from 8 g. of bromobenzene and 1.4 g. of magnesium to a warm solution of 2.7 g. of the "yellow compound" in benzene. A powdery yellow precipitate (ROMgBr compound) first formed and then went into solution as the mixture was refluxed. After heating for one hour the mixture was worked up in the usual way and the product recovered from the benzene–ether extract. After washing out a small amount of oil with ether, a good yellow product was obtained. The substance dissolves readily in glacial acetic acid or toluene and forms a crust of fairly good yellow crystals from the latter solvent; m. p. 247°. The yield was poor, 1.8 g. The material dissolves slowly on boiling with alkali and is precipitated unchanged on acidification. A deep red color is imparted to cold, concentrated sulfuric acid.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.79; H, 4.58. Found: C, 82.20, 82.10; H, 4.72, 4.73.

The substance forms a *diacetate* when treated with acetic anhydride and sodium acetate: small colorless prisms from alcohol melting at 224°.

Anal. Calcd. for $C_{28}H_{20}O_5$: C, 77.04; H, 4.62. Found: C, 76.99, 76.91; H, 4.95, 4.88.

2. Oxidation of the Yellow Condensation Product

Lactone of Benzhydrol-2,3,2′-tricarboxylic Acid (XI).—Fifty-five grams of the "yellow compound" (crude) was dissolved by boiling in a mixture of 2 liters of water and 150 cc. of 6 *N* sodium hydroxide. The flame was removed and 160 g. of potassium permanganate was added in small portions as rapidly as the rather vigorous reaction would allow. The permanganate at first became decolorized as rapidly as it was added, but toward the end a strong purple color persisted. To complete the oxidation the mixture was heated for one-half hour on the steam-bath. It was then cooled in ice and treated with a rapid stream of sulfur dioxide. As soon as the manganese dioxide had dissolved, a colorless salt of the oxidation product began to separate. When there appeared to be no increase in the amount of this material, it was collected, dissolved in hot water, and the clarified solution was acidified. The acid separated in the form of its lactone, and in nearly pure condition; yield, 30 g.

The substance is insoluble in xylene, very readily soluble in alcohol. It crystallizes from dilute alcohol in the form of long, fine, colorless needles melting sharply at 214° with conversion to the anhydride.

Anal. Calcd. for $C_{16}H_{10}O_6$: C, 64.42; H, 3.38. Found: C, 64.42; H, 3.79. *Neut. equiv.* Subs., 0.1939 g., 0.1866 g.: 6.04, 5.67 cc. of 0.2232 *N* $Ba(OH)_2$. Calcd. for $C_{14}H_8O_2(COOH)_2$: 5.84, 5.60 cc.

The anhydride was obtained by heating the acid at a temperature slightly above the melting point until no more water was given off. The material was then distilled and crystallized from benzene–ligroin as small tufts of micro-needles, m. p. 205°.

Anal. Calcd. for $C_{16}H_8O_5$: C, 68.57; H, 2.88. Found: C, 68.65; H, 3.33.

The dimethyl ester, prepared by the use of diazomethane, crystallized from alcohol as stout needles melting at 149°.

Anal. Calcd. for $C_{18}H_{14}O_6$: C, 66.24; H, 4.32. Found: C, 66.14; H, 4.57.

Dilactone of Benzophenone-2,3,2′-tricarboxylic Acid (XII).—The oxidation of the above lactone, XI, was carried out by heating under the reflux condenser a mixture of 30 g. of the substance, 500 cc. of water, 150 cc. of 6 *N* sodium hydroxide and 25 g. of potassium hydroxide. The reaction was completed in two hours. The manganese dioxide was reduced as before, but there was no separation of a salt of the oxidation product. The clarified solution was made strongly acid with hydrochloric acid and evaporated to about two-thirds its volume on the steam-bath. As the sulfur dioxide was expelled, the oxidation product began to deposit from the warm solution. The crude product was dissolved in sodium carbonate solution for purification. When this solution was acidified in the cold there was no precipitate, the free tricarboxylic acid being very soluble in water. Placed on the steam-bath, it slowly deposited excellent crystals of the dilactone in a high state of purity; yield, 22.7 g.

The compound is extremely soluble in alcohol and insoluble in the hydrocarbon solvents. It is readily soluble in ethyl acetate but dissolves slowly and comes out slowly. It formed colorless needles melting at 230°.

Anal. Calcd. for $C_{16}H_8O_6$: C, 64.86; H, 2.72. Found: C, 65.00; H, 3.15.

The methyl ester, prepared by diazomethane, formed star-shaped clusters of small needles from dilute methyl alcohol, m. p. 186.5°.

Anal. Calcd. for $C_{17}H_{10}O_6$: C, 65.80; H, 3.25. Found: C, 65.40; H, 3.70.

Identification of the Oxidation Products.—Since the further degradation products have all been described by Graebe and Juillard,[8] it will be sufficient to describe briefly the methods by which they were obtained and to record the properties noted and the analyses. The latter information is summarized in Table I.

The monobasic dilactone, XII, was converted into the dilactone of benzophenone-2,2′-dicarboxylic acid (XIII), by heating it in a two-bulb distilling flask with about 0.5% of its weight of copper powder (100-mesh, precipitated) at 300° until the rapid evolution of carbon dioxide abruptly ceased. The material was then distilled at diminished pressure and crystallized from alcohol; yield, 92%. The dimethyl ester of the free acid was obtained by dissolving the dilactone in a small quantity of alcoholic alkali, carefully neutralizing the cooled solution and adding an ethereal solution of diazomethane. The ester was recovered from the ether, distilled and crystallized from ether and petroleum ether.

The reduction of the dilactone, XIII, to the lactone of benzhydrol-2,2′-dicarboxylic acid, XIV, was accomplished by heating a solution of the material (4 g.) in alkaline solution (100 cc. of water, 10 cc. of 6 *N* NaOH) with zinc dust (10 g.) for ten hours on the steam-bath. The yield was quantitative and the material, after being dissolved in soda solution and precipitated, was directly pure. The substance was found by mixed melting point determination to be identical with a sample prepared according to Graebe and Juillard.

The final reduction to diphenylmethane-2,2′-dicarboxylic acid was the result of an attempt to cleave the lactone, XIV, by alkali fusion. One gram of the lactone was stirred into 10 g. of molten potassium hydroxide. Lumps of the potassium salt were first formed; the temperature was raised until this had all dissolved to give a clear melt. On dissolving this in water, precipitating the product with acid, and crystallizing it from dilute alcohol, 0.35 g. of the pure dibasic acid was obtained.

Table I

Degradation Products

	Carbon, %		Hydrogen, %		Melting point, °C.	
	Calcd.	Found	Calcd.	Found	F.	G. and J.
Dilactone of benzophenone-2,2′-dicarboxylic acid (XIII)	71.42	71.17	3.20	3.78	211	212
Dimethyl benzophenone-2,2′-dicarboxylate	68.44	68.32	4.73	4.85	82	86
Lactone of benzhydrol-2,2′-dicarboxylic acid (XIV)	70.85	70.87	3.97	4.36	202	203
Methyl ester of XIV	71.62	71.52	4.51	4.76	156	155
Diphenylmethane-2,2′-dicarboxylic acid (XV)	70.30	70.37	4.71	5.18	250	254.5

3. Experiments Relating to the Synthesis of the Yellow Condensation Product

2-[2′-Hydroxynaphthoyl-1′]-benzoic Acid (III).—The most satisfactory method found for the preparation of this acid or of its lactone is as follows. A mixture of 14.8 g. of phthalic anhydride and 15.8 g. of β-methoxynaphthalene was dissolved in 200 cc. of tetrachloroethane at the temperature of the steam-bath. In the course of one hour 25 g. of aluminum chloride was added in small portions, the mixture was shaken occasionally and the heating was continued for one hour more. A clear, deep red-green solution resulted. The aluminum compound was decomposed with ice and hydrochloric acid and the solvent was removed by steam distillation. A thick oil separated when the residue was cooled, the liquor was decanted from the oil and the latter was washed with water. It was found convenient to isolate the acid present in this oil in the form of its lactone. The oil was taken up in acetic anhydride and the solution, after adding fused sodium acetate, was heated on the steam-bath for one-half hour. On cooling the solution the lactone separated in the form of excellent long needles. Washed with a little alcohol and then with water, the substance was very nearly pure; yield, 14 g.

To obtain the free acid, the lactone was dissolved in warm alcoholic alkali, the solution was diluted with water and acidified. Since the acid normally separated in an oily condition, it was extracted with benzene and recovered by concentrating the solution and adding ligroin. From this solvent-pair the acid separates in the form of clusters of pale yellow needles. It melts at 155°, with some softening at a few degrees below that temperature. The alkaline solution is yellow.

Anal. Calcd. for $C_{18}H_{12}O_4$: C, 73.95; H, 4.14. Found: C, 73.82, 73.80; H, 4.47, 4.42.

The lactone may be obtained either by heating the acid or by dehydration with acetic anhydride. The latter reaction is catalyzed by sodium acetate. The compound dissolves readily in benzene and forms long, slender, colorless needles from this solvent; m. p. 195°.

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.81; H, 3.68. Found: C, 78.88, 78.84; **H, 3.99**, 3.96.

The substance is easily converted into the isomeric "yellow compound," m. p. 198°. The addition of aluminum chloride to a hot solution of the lactone in benzene causes the rapid development of a deep red color. This fades within a few minutes to yellow-orange and oily material separates. On decomposing the product with dilute hydrochloric acid and boiling off the benzene, the yellow condensation product is obtained in a high state of purity and in quantitative yield.

The methyl ether was obtained as the chief reaction product when the condensation of phthalic anhydride and β-methoxynaphthalene was carried out in the manner described above but at a lower temperature. The reaction mixture was stirred without external heating for three and a half hours. It warmed slightly of itself and acquired a deep orange color. The crude reaction product was a thick oil. When this was taken up in ether and dried with sodium sulfate, the methoxynaphthoylbenzoic acid soon began to deposit, and further portions were obtained by evaporating the mother liquor. Washed free of inorganic material with water and crystallized from toluene, the ether formed thick, pale yellow needles melting at 196°; yield, 24%.

Anal. Calcd. for $C_{19}H_{14}O_4$: C, 74.49; H, 4.61. Found: C, 74.44, 74.40; H, 4.69, 4.73.

The ether was easily demethylated by heating gently a benzene solution of 1 g. of material with 4 g. of aluminum chloride for three hours. The hydroxynaphthoyl benzoic acid, in pure condition, was the sole reaction product. This shows that the free acid, unlike its lactone, is not easily converted into the "yellow compound."

Other Derivatives.—While the coupling tests referred to in the theoretical part of the paper furnish adequate evidence of the structure of the hydroxynaphthoylbenzoic acid, some attempts were made to establish a more rigorous proof. The acid was heated with copper powder in the hope of effecting a decarboxylation, but the substance, instead of losing carbon dioxide, was cleaved into β-naphthol and phthalic acid. The methyl ether behaved in the same way. Each compound was then reduced to the corresponding naphthylbenzoic acid by means of zinc dust and alkali (quantitative yields), and the decarboxylation of these compounds was attempted. The hydroxy compound, however, was only converted into a lactone and the methyl ether did not lose carbon dioxide at a temperature at which deep-seated decomposition set in. The properties of the compounds in question are listed in Table II, together with two other derivatives of the acid III.

TABLE II

DERIVATIVES OF HYDROXYNAPHTHOYLBENZOIC ACID (III)

	Description	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	M. p., °C.
Methyl ester	Pale yellow prisms	74.49	74.71	4.61	5.13	131
Methyl ether-methyl ester	Pale yellow needles	74.98	74.44	5.04	5.22	109
2-[2′-Hydroxynaphthyl-1′]-benzoic acid	Small needles	77.67	77.92	5.07	5.37	187
Lactone	Prisms	83.05	82.68	4.65	4.93	147
2-[2′-Methoxynaphthyl-1′]-benzoic acid	Prisms	78.05	77.80	5.52	5.69	196

4. The Preparation of 4-Hydroxybenzanthrone (VIII)

The preparation of this compound by the Scholl condensation has been mentioned by Fierz-David and Jaccard[6] but it is described only in the dissertation of the latter.[9]

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[9] Jaccard, Dissertation, Zurich, 1928.

The condensation has been patented,[10] and it has been employed further by Pieroni,[11] who, however, was undecided as to whether the product obtained was a hydroxybenzanthrone or α,β-naphthophenoxanthone. No comparison appears to have been made with the "4-hydroxybenzanthrone" obtained by Perkin and Spencer[12] by the Bally–Scholl reaction. In view of this uncertainty, it may be of value to record the present observations.

1-Benzoyl-2-naphthol was obtained, along with its methyl ether, by condensing benzoyl chloride and β-methoxynaphthalene in tetrachloroethane solution at 25° by means of aluminum chloride. The crude product was distilled and the products separated with alkali. The results may be summarized as follows.

Hydroxy compound (53% yield): yellow needles from alcohol, m. p. 142°. *Anal.* Calcd. for $C_{17}H_{12}O_2$: C, 82.23; H, 4.88. Found: C, 82.24; H, 5.08.

Methoxy compound (22% yield): colorless plates from ligroin, m. p. 1277. *Anal.* Calcd. for $C_{18}H_{14}O_2$: C, 82.41; H, 5.38. Found: C, 82.18; H, 5.38.

The Scholl condensation was carried out by melting together 60 g. of aluminum chloride and 15 g. of sodium chloride, introducing 10 g. of 1-benzoyl-2-naphthol, and heating for two hours at 200°. On pouring the hot melt into dilute hydrochloric acid, a clean, granular product was obtained. In order to reoxidize any reduced material, air was bubbled through a suspension of the substance in alkali for two hours. The residue undissolved by alkali then was dried and distilled, giving 5 g. of good yellow material. The compound forms long, golden-yellow needles from glacial acetic acid, melts at 179°, and is only slightly soluble in boiling alkali.

Anal. Calcd. for $C_{17}H_{10}O_2$: C, 82.91; H, 4.10. Found: C, 82.92; H, 4.45.

Acetate: yellow needles from alcohol, m. p. 158°. *Anal.* Calcd. for $C_{19}H_{12}O_3$: 79.15; H, 4.20. Found: C, 79.62; H, 4.45.

The substance corresponds in every respect with the compounds described by Jaccard and by Perkin and Spencer. The formation of an acetate and of an ethyl ether[12] rules out the alternate structure suggested by Pieroni, and the two different methods of synthesis establish definitely the structure of 4-hydroxybenzanthrone. It is a matter of interest that the addition of boroacetic anhydride causes only a slight deepening in the color of the yellow solution of the substance in acetic anhydride. From this observation it would appear that the Dimroth test is not applicable to α-hydroxybenzanthrones.

5. The Action of Aluminum Chloride on α-Naphthoyl Benzoic Acid (Compound X?)

Very poor results were obtained on following the patent specifications[7] for the intramolecular condensation of α-naphthoylbenzoic acid. Some improvement was made by using the methyl ester of the acid and heating the sodium aluminum chloride melt to a temperature of 130° for two hours, but the results were still far from satisfactory, the yield of pure product being only about 10%. After removing the naphthanthraquinone from the reaction production by vatting, the crude material was precipitated once from its solution in alcoholic alkali, distilled, and crystallized from ligroin. Long, colorless needles melting at 177° were thus obtained.

Anal. Calcd. for $C_{18}H_{10}O_2$: C, 83.70; H, 3.91. Found: C, 83.70; H, 4.41.

As already noted, the substance dissolves easily in cold alcoholic alkali, but it does not appear to be affected by boiling aqueous alkali. It was recovered unchanged after prolonged treatment with diethyl sulfate in alcoholic alkaline solution.

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[10] English Patent 248,791 (1926).

[11] Pieroni, *Chem. Centr.*, II, 308 (1929).

[12] Perkin and Spencer, *J. Chem. Soc.*, **121**, 474 (1922).

6. Note Regarding the Condensation of Phenols with Phthalic Anhydride

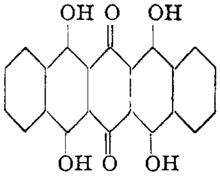
The condensation of phthalic anhydride and β-naphthol in the manner described in the Bayer patent,[2] that is, at a high temperature and with an excess of phthalic anhydride as the solvent, does not give the product claimed, but it does afford an excellent method of preparing the "yellow compound" whose structure is discussed in this paper. It is a matter of interest to know if the method is capable of general application and if the other substances mentioned in the patent have the structures there claimed. As a first step in answering these questions, I have condensed phthalic anhydride with leuckoquinizarine, following the patent procedure. The product obtained has indeed properties entirely consistent with the structure of a tetrahydroxy-bis-lin.-dibenzanthraquinone. From nitrobenzene it forms glistening, deep green needles of great beauty. No melting point was observed.

Anal. Calcd. for $C_{22}H_{12}O_6$: C, 70.96; H, 3.25. Found: C, 70.75, 70.65; H, 3.55, 3.57.

The presence of four hydroxyl groups is established by the formation of a **tetraacetate** on acetylation in the presence of pyridine. The compound formed good orange needles from acetic anhydride and melted with decomposition at 315°.

Anal. Calcd. for $C_{30}H_{20}O_{10}$: C, 66.65; H, 3.73. Found: C, 66.58; H, 3.85.

The green hydroxyquinone forms a red solution in nitrobenzene and it is practically insoluble in the usual solvents. The solution in concentrated sulfuric acid has an intense greenish blue color. The compound dissolves to only a very slight extent in alcoholic alkali but imparts a blue color to the solution. In the appearance of the crystals and in all of the color tests noted, the compound strikingly resembles 1,4,5,8-tetrahydroxyanthraquinone. A sample of the latter substance, prepared in the laboratories of the I. G. Farbenindustrie A.-G., was very kindly made available through the courtesy of Professor J. von Braun. The only qualitative method found for distinguishing the two substances is by means of the Dimroth test. Heated with acetic anhydride and boroacetic anhydride, the anthraquinone gives a purple solution with a dull red fluorescence; the dibenzanthraquinone derivative gives a blue solution with a brilliant red fluorescence of great beauty. On account of the general similarity of the two compounds, it appears probable that the new substance has the structure of 1,4,5,8-tetrahydroxy-2,3,6,7-dibenzanthraquinone, XX.



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Summary

A study has been made of an interesting compound which is formed by condensing β-naphthol with phthalic anhydride in the presence of aluminum chloride. The reaction does not appear to belong to any of the known types, and the problem of ascertaining the structure of the compound produced has been a perplexing one. A study of the properties of the substance, of the step-wise synthesis, and of the degradation of the compound by oxidation has led to the rejection of a structural

formula which has just been proposed by investigators working on the same problem in another laboratory, and it has led to the conclusion that the facts are best represented by the structure shown in formula XIX.

Converse Memorial Laboratory
Cambridge, Massachusetts

NOTE

A Method for the Preparation of Diethyl Oxalate.—In the preparation of ethyloxalacetic ester which was used in the synthesis of thymine to be reported later, considerable amounts of diethyl oxalate were needed. The present paper reports a somewhat simpler method than the most satisfactory ones now employed which gives correspondingly high yields. The removal of any water already present and of that formed during esterification, which is essential for the completion of the coupling between oxalic acid and ethyl alcohol, is brought about by a preliminary distillation of alcohol from the mixture whereby the water is carried over in the distillate with the alcohol. Clarke[1] employs a ternary mixture of alcohol, water and carbon tetrachloride to bring this about, while Kenyon[2] resorts to a continuous drying of the water laden alcohol with anhydrous potassium carbonate and the return of the dried alcohol vapor to the flask containing the reactants. In our method sufficient of the water has been removed by the preliminary distillation so that after the addition of a second lot of alcohol the esterification is almost quantitatively completed.

Experimental.—One kilogram of c. p. crystalline oxalic acid ($(COOH)_2 \cdot 2H_2O$) and 2 liters of absolute alcohol are heated on a water-bath with a reflux condenser until solution is effected (usually about two hours). The mixture is subjected to vacuum distillation (25 mm.) on a water-bath at 80° until the temperature of the vapors reaches about 60°. At this point a considerable quantity of unesterified oxalic acid crystallizes out on the sides of the flask. About 35% of the oxalic acid is in the form of diethyl ester. Two liters of absolute alcohol are mixed with the ethyl oxalate, oxalic acid and the small amount of ethyl alcohol remaining in the flask. This is refluxed for three hours. The excess alcohol containing most of the balance of the water is again removed by distillation under diminished pressure. The remaining ester is dried overnight with anhydrous sodium sulfate, filtered and distilled. The fraction boiling at approximately 97°

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[1] Clarke, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II, p. 22.

[2] Kenyon, *ibid.*, **1925**, Vol. V, p. 59.