plex has been isolated and the sulfinic acid, after being dislodged from the cobalt, crystallized as such. In colorless solutions this reaction can be used as a sensitive test for hydrogen peroxide.

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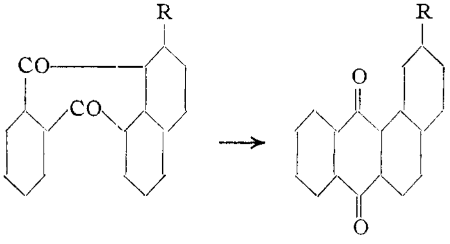
The Conversion of Phthaloylnaphthalenes and Naphthoyl-2-benzoic Acids into Benzanthraquinones[1]

BY LOUIS F. AND MARY FIESER

According to a recent patent[2] 1,8-phthaloyl-2-naphthol, I ($R = OH$), rearranges when heated with sulfuric acid to give an hydroxy-1,2-benzanthraquinone which probably has the structure of II.



I II

It seemed to us a matter of interest to study this reaction further, both for the purpose of establishing the course of the reaction and the structures of the quinones mentioned but not described in the patent, and with the idea of gaining further evidence of the structures of the benzanthraquinones previously obtained by us[3] by the action of aluminum chloride on methylated naphthoyl-2-benzoic acids.

If the rearrangement follows the course indicated, 2-methyl-1,8-phthaloylnaphthalene, I ($R = CH_3$), a compound which we recently obtained synthetically,[4] would be expected to yield 2′-methyl-1,2-benzanthraquinone. The product is indeed identical with a quinone which was first prepared by Cook,[5] and to which he assigned the structure indicated with the reservation that the evidence rendered this structure very probable, but not certain. Since there remained some element of doubt in the matter, we turned to the dimethyl derivatives. The first of these to be considered was the phthaloylnaphthalene ("pleiadenedione") derivative, VIII, which we had previously synthesized[4] from 2,6-dimethylnaphthalene,

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(1) Sixth paper.

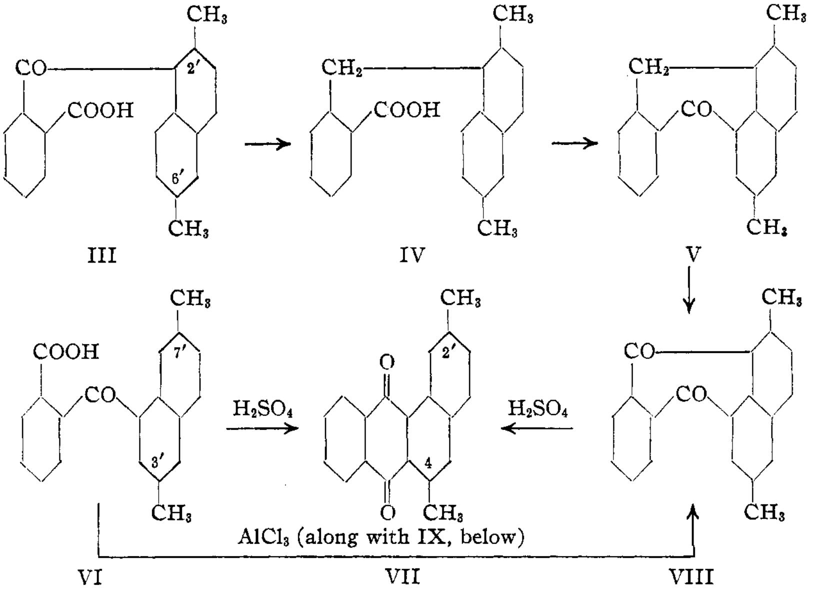
(2) I. G. Farbenind., German Patent 555,081 (1932).

(3) Fieser and Peters, THIS JOURNAL, **54**, 3742 (1932).

(4) Fieser and Fieser, *ibid.*, **55**, 3010 (1933).

(5) Cook, *J. Chem. Soc.*, 2551 (1929).

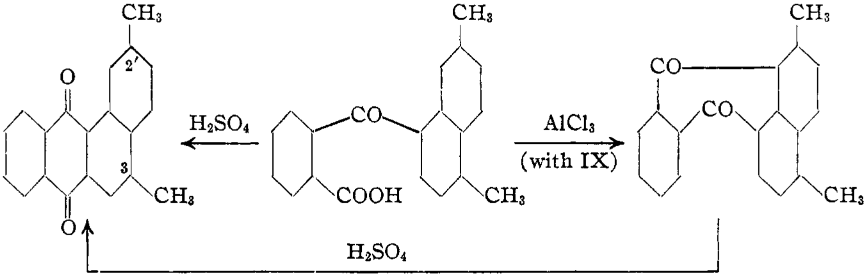
through the series: III ⟶ IV ⟶ acid chloride ⟶ V ⟶ VIII. The rearrangement of VIII with sulfuric acid would be expected to yield VII, but the quinone produced was not identical with the substance previously obtained[3] by the action of aluminum chloride and sodium chloride on the keto acid III and regarded by us as probably having the structure of VII.



In order to clear up this matter an effort was made to prepare VII by an independent method which would be free from any uncertainty. Since the keto acids resulting from the reaction of phthalic anhydride with the methylated naphthalenes are always obtained in pure condition from the reaction mixture only with difficulty, it seemed probable that III might be accompanied by an isomeric acid. A careful study of the condensation product indeed led to the isolation of a keto acid which will be shown to have the structure of VI. Unlike the isomer III, VI is converted by sulfuric acid into a dimethylbenzanthraquinone, and this proved to be identical with the quinone obtained by rearrangement of the diketone, VIII. The quinone in question must have the structure of VII, for no other dimethylbenzanthraquinone can be derived from 2,6-dimethylnaphthalene without a methyl migration. The reactions used in the preparation, namely, the Friedel and Crafts reaction at 0° and sulfuric acid ring closure, are not such as to permit a migration. This evidence thus serves to establish the course of the rearrangement of the phthaloylnaphthalenes.

Regarding the isomeric keto acid which we have defined as VI, it will be observed that only two structures are possible: that indicated and that in which the phthalic acid residue is attached in the β-position. Our reason for preferring the former structure is that when heated with sodium aluminum chloride the acid yields, in addition to a considerable amount of a dimethylbenzanthraquinone, a small amount of the diketone, VIII. Such a reaction might be regarded at first sight as a dubious basis for the assignment of structure, particularly since there is a migration of both a methyl and a ketone group in the formation of the quinone produced (see below). The evidence nevertheless appears to be valid. The identity of the diketone with the synthetic product, VIII, shows that there is no methyl migration in this case, and evidence to be presented below shows that a carboxy-benzoyl group does not migrate from a β- to an α-position under the conditions of the reaction. The diketone, VIII, thus must come from the α-keto acid, VI, as indicated in the formulas. In connection with our synthesis of phthaloylnaphthol,[4] it may be pointed out that a derivative of phthaloylnaphthalene (VIII) now shown to be produced by the method of the I. G. Farbenindustrie[6] has also been prepared by a reliable synthesis.

It will be evident that the quinone obtained from III in the sodium aluminum chloride melt must have some structure other than that (VII) previously assigned. We are now fortunate in being able to identify it as 2′,3-dimethyl-1,2-benzanthraquinone, IX, which was prepared for comparison in the following manner. From the condensation of phthalic anhydride with 1,6-dimethylnaphthalene there was obtained a keto acid to which we assign the structure X. The evidence is that the acid yields the



diketone, XI (along with IX), when condensed by means of aluminum chloride. The carboxy-benzoyl group must be in an α-position, the adjoining peri-position must be free, and the ortho position must also be unoccupied (for the acid yields a quinone with sulfuric acid). No formula other than X meets these specifications, hence the product of ring closure with sulfuric acid must be IX.

The action of aluminum chloride on the keto acid III is thus more complicated than was supposed at the time of our earlier investigation. The formation of IX must be the result both of a migration of the keto group

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[6] English Patent 303,375 (1930).

and of a displacement of a methyl group out of the position adjacent to the quinone ring into a position one more carbon removed. The displacement is entirely comparable with that observed by Mayer and coworkers,[7] in the formation of methylated benzanthrones by the Scholl reaction. A similar shift of a methyl group occurs in the condensation of the isomeric acid, VI, even though there probably is no migration of the keto group in this case. It is of interest that no methyl migration takes place in the formation of the diketones, VIII and XI, in the reactions which lead also to the production of the quinone, IX, with a shifted methyl group. It may be noted further that the quinone VII, which would be the normal reaction product, is stable under the conditions of the experiment. It may be inferred that the methyl wandering occurs either during the migration of the keto group or during ring closure.

The search for isomers in the Friedel and Crafts reaction with phthalic anhydride was most fruitful in the case of 2,3-dimethylnaphthalene, for all of the three possible keto acids were isolated: formulas XII, XV and XVIII. The structure of the first of these follows from the fact that it yields no quinone with sulfuric acid. The second one, XV, is an α-keto acid, for it is condensed by aluminum chloride in part to a phthaloylnaphthalene derivative, XVII. A methyl migration is involved in the reaction, for the substance is isomeric with XIV, which was previously prepared from XII by the standard synthesis. The third acid, XVIII, is evidently a derivative of β-naphthoylbenzoic acid, for by the action of aluminum chloride it is converted partly into a 1,2-benzanthraquinone, XVI (which vats), but partly also into a mixture containing at least two 2,3-benzanthraquinone derivatives, XIX (which do not vat with aqueous hydrosulfite, but which are distinguished from the diketones XIV and XVII by reversible reduction in an alcoholic medium). The behavior of this compound, which is the only β-acid we were able to study, gives us confidence that the method which we have employed to distinguish between α and β acids is a valid one in spite of its drastic nature.

It will be observed from the chart that the acids XV and XVIII yield 2'3'-dimethyl-1,2-benzanthraquinone (XVI) on ring closure with sulfuric acid, and that the same quinone can be obtained from the third keto acid, XII, by conversion into XIV and rearrangement. This quinone also is always present in the mixture of products obtained by the action of aluminum chloride on any of the three keto acids. The structure originally assigned to the condensation product from XII is thus correct, and the chief reaction product is formed without methyl migration in this case in which no alkyl group can appear adjacent to the quinone nucleus. It should be made clear, however, that the aluminum chloride condensations are never clean-cut, that the yields are poor and that the quinones formed are ob-

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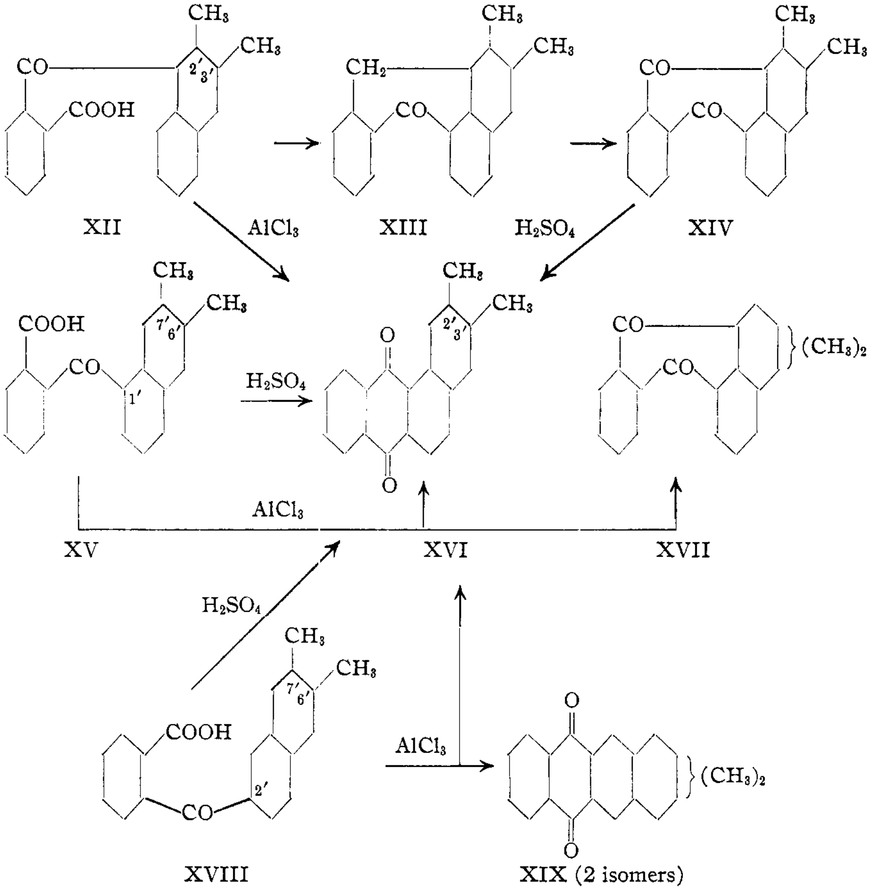
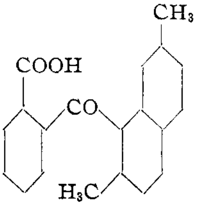
[7] Mayer, Fleckenstein and Günther, *Ber.*, **63**, 1464 (1930).

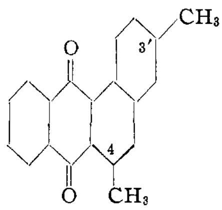


tained in a pure condition with great difficulty, if at all. Thus the samples of the quinone XVI resulting from any of the reactions involving sulfuric acid were far purer than could be obtained in the aluminum chloride condensations. The latter type of reaction may be of some theoretical interest but is without practical value.

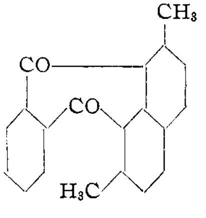
There remains for consideration one other compound mentioned in our earlier paper. It was obtained from XX with aluminum chloride and



XX



XXI



XXII

described as 3′,4-dimethylbenzanthraquinone, XXI. We can now declare this structure incorrect, for the substance is not identical with the true compound corresponding to XXI. This was obtained by the action of sulfuric acid on an isomer of XX which was isolated in too small a quantity to permit a decision between the two possible structures. Both isomers, however, would yield the same quinone. In this connection it may be noted that phthaloyl-2,7-dimethylnaphthalene, XXII, does not rearrange to a quinone when heated with sulfuric acid. This shows that a free position adjacent to one of the carbonyl groups is required for such a rearrangement.

Experimental Part[8]

1. **The Methylated Naphthoyl-2-benzoic Acids.**—The Friedel and Crafts reaction of phthalic anhydride with the various methylated naphthalenes was carried out at 0° in tetrachloroethane solution in the manner described in the earlier paper[3] but on a five-fold scale. The new isomers isolated and their esters are for the most part listed in Tables I and II, and it will be only necessary to make a brief statement of the methods of separation employed.

TABLE I

DIMETHYL-1′-NAPHTHOYL-2-BENZOIC ACIDS

Positions of substituents	Formula	Melting point, °C.	Description	Analyses, % C Calcd.: 78.92	Analyses, % H Calcd.: 5.30
3′,7′	VI	225	Micro crystals	78.79	5.52
4′,7′	X	189	Small needles	78.62	5.21
2′,3′	XII	229	Prisms	78.46	5.30
6′,7′	XV	234	Large prisms	78.57	5.33
DIMETHYL-2′-NAPHTHOYL-2-BENZOIC ACID					
6′,7′	XVIII	193	Needles	78.54	5.04
DIMETHYL-1′(OR 2′)-NAPHTHOYL-2-BENZOIC ACID					
3′,6′		193	Small needles	79.21	5.39

TABLE II

METHYL ESTERS OF DIMETHYL-1′-NAPHTHOYL-2-BENZOIC ACIDS

Positions of substituents	Melting point, °C.	Description	Analyses, % C Calcd.: 79.23	Analyses, % H Calcd.: 5.70
3′,7′	110	Thick needles	79.27	5.93
6′,7′	125	Prisms	79.15	5.63
METHYL ESTER OF DIMETHYL-2′-NAPHTHOYL-2-BENZOIC ACID				
6′,7′	145	Prisms	79.23	5.84
METHYL ESTER OF DIMETHYL-1′(OR 2′)-NAPHTHOYL-2-BENZOIC ACID				
3′,6′	85	Prisms	79.46	5.84

From 2,6-Dimethylnaphthalene.—The crude keto acid was esterified by boiling with methyl alcohol and sulfuric acid and the solution on cooling deposited a large crop of the ester of 2′,6′-dimethylnaphthoyl-2-benzoic acid (m. p., pure, 162°)[3] in nearly pure condition. From the mother liquor, after suitable concentration, more of this

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(8) For the analyses here reported we are greatly indebted to Dr. C. Harold Fisher.

ester crystallized, along with some long, thick needles of the 3′,7′-isomer (m. p. 110°). On account of the unusual size of these crystals, it is easy to pick them out of the mixture. It is also possible to dissolve out the less soluble isomer, leaving the large crystals for the most part unchanged.

A fairly sharp separation is thus not difficult, and the yields, based upon the amount of dimethylnaphthalene used, were as follows: 2′,6′-ester, 47%; 3′,7′-ester, 20%. The corresponding acids were prepared by hydrolysis of the pure esters and the new one, VI, was crystallized from either alcohol or benzene. It is more soluble than the isomer previously described, m. p. 238°. As a further check on the structure of the latter compound, it was converted by decarboxylation into 1-benzoyl-2,6-dimethylnaphthalene,[9] which was found to be identical with an authentic sample.

From 1,6-Dimethylnaphthalene.—The reaction product in this case consisted very largely of the 4′,7′-acid, m. p. 189°, which was the only isomer isolated. Fractional crystallization of the ester was not possible, for the crude acid on esterification gave only an oil. The crude acid, m. p. 165–175°, was thus crystallized repeatedly from toluene. On very slow cooling, the solution deposited large prisms containing solvent of crystallization. The last crystallizations were from ethyl acetate.

From 2,3-Dimethylnaphthalene.—The reaction of this hydrocarbon leads to a mixture of three isomers and a separation by fractional crystallization of either the acid mixture or the ester mixture is extremely tedious. Once the compounds had all been isolated, however, it was possible to work out a fairly simple procedure on the basis of the properties noted. The crude acid mixture was dissolved in alkali, and the solution was cooled, treated with an excess of alkali and rubbed vigorously against the walls, when a part of the material separated in the form of the sodium salt. Once separated from the mother liquor, the salt was sparingly soluble and crystallized well. After three crystallizations, it was converted to the acid, which was the pure 3′,7′-isomer, XII. The sample of this acid, crystallized from toluene, was much better than that obtained in our earlier work and the new data reported in the table replace the earlier observations.

After removing all of the sodium salt which could be caused to separate from the alkaline solution, the material in the mother liquor was converted into the free acid, which was thoroughly dried and powdered. We then took advantage of the fact that the 6′,7′-α-acid is higher melting, and less soluble than the 6′,7′-β-acid. On boiling the mixture with benzene, it was found that about half of it dissolved easily in this solvent while the remainder dissolved with such difficulty that it was easily separated. This residue consisted almost entirely of the α-acid, which was obtained in a completely pure condition by crystallization from glacial acetic acid. The benzene mother liquor was evaporated to dryness and the acid was esterified. It will be observed that the melting point relationship of the α and β esters is just the reverse of that of the acids, and the same is true of the solubilities. Thus on crystallization of the end fraction in the form of the ester, it was not difficult to obtain the β-ester in a pure condition. The β-acid obtained on hydrolysis crystallized well from benzene. The yields of pure products were as follows: 2′,3′-α-acid, 35%; 6′,7′-α-acid, 17%; 6′,7′-β-acid, 7.3%.

From 2,7-Dimethylnaphthalene.—The reaction product consisted very largely of the 2′,6′-acid, XX,[3] but the collection of the bulk of this material in a pure condition is a tedious matter. We crystallized the material for a time as ester and obtained several crops of pure material from alcohol, m. p. 131°. It then became more profitable to crystallize the material in the form of the acid from benzene, and this gave a few crops of pure acid, m. p. 210°. Suffice it to say that a point was eventually reached when only traces of the 2′,6′-acid or its ester could be extracted and the amounts collected represented a 75% yield of this isomer. At this point the isomeric 3′,6′-acid,

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(9) Cook, *J. Chem. Soc.*, 456 (1932).

m. p. 193°, could be isolated in the form of its sodium salt. Once the proportion of this isomer in the mixture becomes appreciable, the sodium salt separates readily, and since it is only sparingly soluble in water it is easily purified. The free acid was then crystallized from benzene–ligroin. The yield amounted to just 1%. The methyl ester was prepared from the pure acid with diazomethane and then distilled, but it was only obtained as a solid by cooling an ethereal solution in a carbon dioxide and ether bath.

From β-Methylnaphthalene.—Two isomers were isolated from the reaction mixture: 2′-methyl-1′-naphthoyl-2-benzoic acid, m. p. 197°, and 7′-methyl-1′(or 2′)-naphthoyl-2-benzoic acid, m. p. 190°. The first of these was described by Scholl as melting at 190–191°,[10] and the same melting point was found in our earlier work.[3] We were able to obtain in the present case the methyl ester as a solid, and to effect a further purification through the crystallization of this derivative. We found no really satisfactory way of extracting this isomer in quantity or of isolating the other isomer. The crude acid was esterified and the oily ester was dried in ether and distilled twice in vacuum. This treatment has the disadvantage that some of the ester of the 190° acid is converted into the corresponding benzanthraquinone, but it at least afforded a means of obtaining the other ester as a solid. The solid ester separated very slowly from a methyl alcoholic solution of the glassy distillate and was easily purified. The material in the mother liquor was hydrolyzed and the acid, on fractional crystallization from benzene, gave first a few crops of the 197° acid in a fairly pure condition and finally a small amount of the 190° isomer. The total yields of completely pure materials amounted to 47 and 3%, respectively.

The methyl ester of 2′-methyl-1′-naphthoyl-2-benzoic acid formed small colorless crystals, m. p. 112°, from methyl alcohol.

Anal. Calcd. for $C_{20}H_{16}O_3$: C, 78.92; H, 5.30. Found: C, 78.79; H, 5.35.

7′-Methyl-1′(or 2′)-naphthoyl-2-benzoic acid, m. p. 190°, formed large, rectangular prisms from benzene. The ester was not obtained as a solid. The structure assigned follows from the conversion of the acid into 2′-methyl-1,2-benzanthraquinone with sulfuric acid.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.75; H, 4.93.

2. The Quinones and Diketones Obtained by Condensation

With Sulfuric Acid.—The quinones listed in Table III-A were all obtained by ring closure of at least one keto acid with sulfuric acid, as explained in the theoretical part of the paper, and their structures are all known with certainty. Table III of our earlier paper[3] should be altered as follows: the descriptions given for the "2′,4-" and the 2′,3′-quinone should be stricken out, for we have now obtained better samples, and the former compound is now shown to be the 2′,3-isomer. The substance described as the "3′,4-" isomer, m. p. 195°, is now shown to be of unknown structure.

For the preparation of the 2′,3′-isomer short heating of the keto acids with concentrated sulfuric acid on the water-bath gave a satisfactory method of ring closure. The blue solution of XV in the cold acid and the brown solution of XVIII both become purple, and a clean yellow product was precipitated with water. For the other ring closures we used 82% sulfuric acid, for the concentrated acid caused too much sulfonation. In preparing IX it was found that it was best to heat the acid solution for one-half hour on the steam-bath; in the other two cases the keto acid (1 g.) was suspended in 10 cc. of the acid and the mixture was heated just to the boiling point over a free flame. On crystallization from glacial acetic acid there was never any difficulty in obtaining a pure sample. Needless to say, each substance was carefully compared with any other samples melting in the same temperature range.

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(10) Scholl and Tritsch, *Monatsh.*, **32**, 997 (1911).

TABLE III

CONDENSATION PRODUCTS

Positions of substituents	Formula	Melting point, °C.	Color in cold H_2SO_4	Analyses, % C Calcd.: 83.89	Analyses, % H Calcd.: 4.93
A. Dimethyl-1,2-benzanthraquinones (yellow needles)					
2′,4	VII	173	Indigo	83.67	4.92
2′,3	IX	203	Indigo	83.79	4.94
2′,3′	XVI	247	Purple	83.69	4.91
3′,4′	XXI	175	Purple	83.81	4.96
B. Dimethyl-1,8-phthaloylnaphthalenes (faintly yellow needles)					
2,5	XI	140	Yellow	83.48	4.83
?,?	XVII	182	Orange	83.72	4.88
C. Dimethyl-2,3-benzanthraquinones (yellow needles)					
?,?	XIXa	230	Blue	83.85	4.96
?,?	XIXb	296	Blue	83.23	4.96

With Aluminum Chloride.—The condensation of the keto acids by means of this reagent is far from smooth. The yields are poor, the products are difficult to isolate and purify, and it is not improbable that other products in addition to those isolated were present in the reaction mixtures. In general we found the following procedure to give the best results. Ten grams of the keto acid was stirred into a melt from 12.5 g. of sodium chloride and 62.5 g. of aluminum chloride at about 100°. The temperature was soon brought to 130° and kept there for one hour. The melt was poured onto ice and the yellow, more or less tarry solid was collected from the cold suspension and digested with alkali. This removed a considerable amount of dark, tarry material. The residue, which on drying was in most cases a solid but dark colored product, usually was then crystallized once from glacial acetic acid in order to concentrate the quinone into the crystalline part and the more soluble diketone, if present, into the mother liquor. The crystalline material on distillation and repeated crystallization eventually yielded a good sample of the quinone. The material recovered from the mother liquor was distilled, precipitated from a solution in glacial acetic acid with water and boiled repeatedly with alkaline hydrosulfite solution. The diketone, if present, was found in the residue from this treatment.

The process was varied somewhat in the experiment with the β-naphthoyl acid, XVIII, for all of the products are of the same degree of solubility. As soon as a good solid was obtained, it was separated into a part which vatted and a part which did not. From the latter part the two substances listed as XIXa and XIXb were isolated by fractional crystallization. We are not certain that either of these is a completely pure compound, and the analysis of the higher melting product indicates such a low carbon value that it is possible that the substance is a monomethyl rather than a dimethyl derivative. That the two substances are derivatives of naphthacenequinone is clearly shown by the following tests. Boiled with aqueous hydrosulfite solution, only a faintly green color develops; in an alcoholic solution the vat is red if only a little water is present, but is green in the presence of more water. Boiled with glacial acetic acid and zinc dust, each quinone gives an eosine-red solution which is rapidly discharged on shaking with the air.

The three phthaloylnaphthalene derivatives obtained from the melts were VIII (for description see Ref. 4), XI and XVII. They were recognized as such by their failure to form a vat and by their solubility in alcoholic alkali, and the first one mentioned was found to be identical with the synthetic material.

The dimethyl benzanthraquinones resulting from these melts were seldom obtained in quite as pure a form as the samples obtained with sulfuric acid. Thus the 2′,3′-derivative prepared by the latter method from XV, which can condense in but one way, melted at 247°. Prepared with sulfuric acid from the β-acid, XVIII, from which two quinones are possible, the melting point was 240°. By the aluminum chloride method, the acids XII, XV and XVIII gave samples melting, after very careful purification, at the following temperatures: 244, 239, 245°.

It seems unnecessary to give any further account of the many transformations indicated in the charts given in the first part of the paper.

3. The Rearrangement of the Phthaloylnaphthalenes

The reaction of the methylated diketones with sulfuric acid in general gives very good results. Without special control for each different compound, there may be some losses through sulfonation or charring, but it is a simple matter to isolate the product in a pure condition, for the reaction apparently proceeds in only one direction and no isomers or by-products are formed. The general procedure was to heat a suspension of 1 g. of material in 10 cc. of 82% sulfuric acid over a free flame until a clear red solution resulted and then until, on reaching the boiling point, this suddenly turned brown and a brown oil separated (one to two minutes). The mixture was then poured into water to precipitate the quinone. The rearrangement of 2,3-dimethylphthaloylnaphthalene (XIV) was particularly smooth; the red solution on being heated further suddenly set to a crystalline paste of the quinone (XVI), and the compound was collected in nearly quantitative yield and melting at 247°.

Most of the rearrangements studied and the products obtained are indicated in the formula charts. The dimethylphthaloylnaphthalene of unknown structure, XVII, gave a quinone of m. p. 223° which was not identified. 2-Methylphthaloylnaphthalene[4] on rearrangement yielded 2′-methyl-1,2-benzanthraquinone, m. p. 189°, identical with the material prepared according to Cook[5] or by the condensation of the keto acid, m. p. 190°, described in Section 1.

2′-Hydroxy-1,2-benzanthraquinone.—For the rearrangement of phthaloylnaphthol itself we found, in agreement with the patent claims,[2] that a somewhat more dilute acid is required. Using a mixture of 5 cc. of concentrated sulfuric acid and 2.5 cc. of water for 1 g. of material, and heating the mixture at the boiling point for a short time in the manner described above, the yield of purified product amounted to about 50% of the theoretical quantity. The crude material was best purified through the acetate. It then crystallized well from alcohol in which it is moderately soluble, forming bright red needles melting at 253°. The solution in sulfuric acid is green; the solution in hot, dilute alkali is deep blue and a purple salt separates on cooling.

Anal. Calcd. for $C_{18}H_{10}O_3$: C, 78.82; H, 3.68. Found: C, 78.82; H, 3.81.

The acetate was prepared by boiling the crude hydroxy quinone with acetic anhydride and a trace of sodium acetate, filtering the solution from some dark residue, and setting it aside to crystallize. The compound is sparingly soluble in glacial acetic acid and forms fine yellow needles melting at 255°.

Anal. Calcd. for $C_{20}H_{12}O_4$: C, 75.93; H, 3.83. Found: C, 75.48; H, 3.77.

2′-Chloro-1,2-benzanthraquinone.—2-Chlorophthaloylnaphthalene[11] (1 g.) was heated with 5.5 cc. of concentrated sulfuric acid at 125° for fifteen minutes and the solution was poured into water. A good product (0.8 g.) was obtained, and for analysis it was distilled in vacuum and crystallized from glacial acetic acid; fine yellow needles, m. p. 233–234°.

Anal. Calcd. for $C_{18}H_9O_2Cl$: C, 73.87; H, 3.10. Found: C, 73.71; H, 3.38.

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[11] L. F. Fieser, THIS JOURNAL, **53**, 3546 (1931).

It seems to us probable that the compound here described is identical with a substance prepared by Heller[12] from the condensation of a keto acid obtained from phthalic anhydride and β-chloronaphthalene. Heller regarded his product as 2′-chloro-2,3-benzanthraquinone because it yielded an anthraquinone-dicarboxylic acid on oxidation. The oxidation product was analyzed, but not identified, and from the description given it might be either the 1,2- or the 2,3-isomer. His chloro compound, however, gave the vat test, which is good evidence that it was a derivative of 1,2-benzanthraquinone. His compound melted at the same temperature as ours (233–234°), hence, considering the structure of his starting material, it is probable that the two compounds are identical.[13]

Summary

Phthaloylnaphthol and a number of methylated derivatives of phthaloylnaphthalene rearrange readily under the influence of sulfuric acid to give 1,2-benzanthraquinones. The structures of the resulting compounds were established by preparing the quinones in a different way, and in the course of this work a careful study was made of the Friedel and Crafts reaction of phthalic anhydride with the methylated naphthalenes. Though the chief product is formed by substitution in an α-position ortho or para to an alkyl group, some reaction occurs at α-positions not so activated, and in one case at an unreactive β-position. The last two types of keto acids yield 1,2-benzanthraquinones on treatment with sulfuric acid, whereas all of the acids react under the influence of aluminum chloride to give mixtures which often contain both benzanthraquinones and phthaloylnaphthalenes. The reaction in some cases involves not only a wandering of the ketonic group, as pointed out in an earlier paper, but a methyl migration.

(12) Heller, *Ber.*, **45**, 665 (1912); **46**, 1497 (1913).

(13) Compare Scholl and Neuberger, *Monatsh.*, **33**, 511 (1912).

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Lycopodiumoleic Acid[1]

BY J. L. RIEBSOMER AND JOHN R. JOHNSON

In an investigation of the spores of *Lycopodium clavatum* Langer[2] reported the presence of approximately 50% of a fatty oil, which he found to consist largely (80–87%) of the glyceride of an acid of the oleic series, $C_{16}H_{30}O_2$. This acid he named lycopodiumoleic acid and from his chemical studies formulated it as α-decyl-β-isopropylacrylic acid (I). In a contemporaneous paper, Bukowski[3] reported the glyceride of oleic acid as the main component (80%) of lycopodium oil and, in addition to small amounts

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(1) This paper is abstracted from a thesis submitted by J. L. Riebsomer to the Graduate Faculty of Cornell University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1932.

(2) Langer, *Arch. pharm.*, **227**, 241, 289, 625 (1889).

(3) Bukowski, Dissertation, Warsaw; *cf. Chem. Z.*, **13**, 174 (1889).