obtained of the temperatures at which breaking of the bond in the various ethanes takes place.

The strength of the ethane bond is affected by the nature of the aryl groups.

The ethane bond is cleaved by hydrogen iodide, by bromine, by sodium–potassium alloy and in some penta-arylethanes by 40% sodium amalgam.

ANN ARBOR, MICHIGAN RECEIVED MARCH 9, 1933
PUBLISHED JULY 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

A Synthesis of Phthaloylnaphthol[1]

BY LOUIS F. AND MARY FIESER

To the yellow substance resulting from the condensation of β-naphthol and phthalic acid in the presence of aluminum chloride,[2] Rieche and Frühwald, in the first recorded investigation of the compound,[3] assigned the structure of 1,8-phthaloyl-2-naphthol (I, below). Since this structure appeared to be out of harmony with certain observations which had been made by one of us, objection was raised to Rieche's views and an alternate formula was suggested.[4] In a more recent study of the interesting yellow compound, Rieche and his collaborators[5] have discovered certain new facts which definitely exclude our formula and which furnish convincing if not altogether satisfying evidence that the substance actually has the structure originally favored by the German investigators. After elimination of the hydroxyl group, the resulting compound was reduced by distillation over zinc dust to a hydrocarbon, and this could be converted into the original diketone by oxidation. Though this is the sole evidence that the compound contains two carbonyl groups, it would furnish a sufficient basis for accepting the Rieche formula were it not for the isolation in this Laboratory[4] of an oxidation product which is difficult to reconcile with the formula under discussion. A secondary oxidation product isolated was assigned the structure III, and the formation of this degradation product is entirely consistent with Rieche's formula, I. A precursor of III, however, was a substance regarded as having the structure of II, and it is not easy to see how this can be formed from I in a permanganate oxidation.

This was our most serious objection to Rieche's formula and, although we must grant that this author has made adequate reply to our other objections, we cannot agree that he is justified in waiving the problem presented by this product of oxidation. He regards the structure as still

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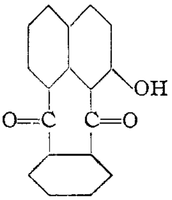
[1] Fifth paper in the series: Condensations and Ring Closures in the Naphthalene Series.

[2] Fr. Bayer and Co., German Patent, 298,345 (1916).

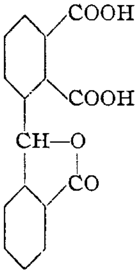
[3] Rieche and Frühwald, *Ber.*, **64**, 1603 (1931).

[4] Fieser, THIS JOURNAL, **53**, 3546 (1931).

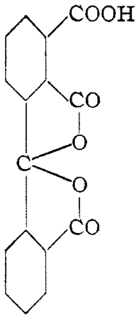
[5] Rieche, Sauthoff and Müller, *Ber.*, **65**, 1371 (1932).



I



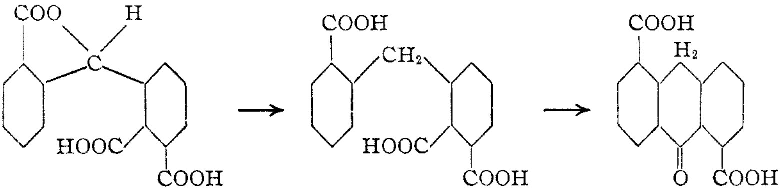
II



III

uncertain and suggests that the acid may have the formula $C_{16}H_{12}O_6$, rather than $C_{16}H_{10}O_6$, though his only evidence for this view is that one of two analyses agrees better with the formula indicating two additional hydrogen atoms. Our empirical formula, however, was based upon analyses not only of the acid, but of two of its well-defined derivatives.

The structure (II) proposed for the dibasic acid was based largely upon oxidation to III and decarboxylation, which gave the dilactone of benzophenone-2,2′-dicarboxylic acid. The position of the carboxyl group eliminated in this way was inferred from the fact that the dibasic acid, II, forms an anhydride. Since this evidence has been questioned, we have made a further study of the acid and we can now report the following additional facts. (1) The oxidation product has been obtained in 75.6% yield. (2) Titrations with alcoholic potassium hydroxide reveal the presence of two carboxyl groups and of one lactone grouping. (3) The monolactone, II, can be obtained in quantitative yield by reduction of the dilactone III with zinc dust in alkaline solution. This corresponds with the similar reduction of the dilactone of benzophenone-dicarboxylic acid.[4,6] (4) On fusion of II with alkali the material is reduced to diphenylmethane-1,2,1′-tricarboxylic acid, IV. The structure of this acid follows from its conversion, in the form of the anhydride, and by the action of fused sodium aluminum chloride, into anthrone-1,5-dicarboxylic acid (V), a substance which has been described by Scholl and Böttger.[7] The result of the alkali fusion is entirely similar to that noted in the case of the lactone of benzhydrol-2,2′-dicarboxylic acid.[4]

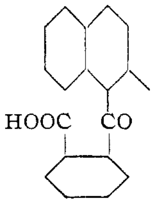


II IV V

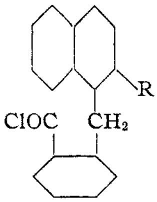
(6) Graebe and Juillard, *Ann.*, **242**, 214 (1887).

(7) Scholl and Böttger, *Ber.*, **63**, 2440 (1930).

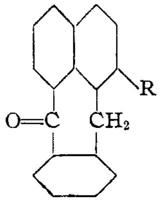
It is obvious that this new evidence only serves to confirm the structure indicated by our previous work. We are thus confronted with a dilemma: either the Rieche formula is incorrect, or the oxidation follows a most remarkable course. Though there is no ground for questioning the evidence of structure presented by Rieche, it seemed to us worth while in view of this perplexing situation to attempt a synthesis of phthaloylnaphthol by a method which would leave no question as to the structure. In a previous paper by the present authors[8] it was shown that keto acids of the type of VI, in which R = CH_3, undergo cyclization under the influence of molten sodium aluminum chloride, but only subsequent to a migration of the phthalic acid residue. It occurred to us that this migration could be prevented and that, at the same time, the ring closure could be facilitated by the reduction of the ketonic group.



VI

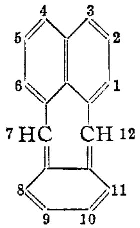


VII

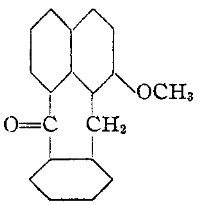


VIII

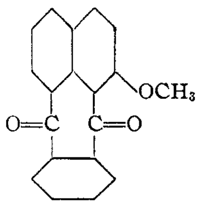
It was indeed found that acid chlorides of the type of VII can be converted in very good yield to the cyclic ketones, VIII, by the action of aluminum chloride in nitrobenzene solution at 0°. The reaction is a general one, for no difficulty was experienced in effecting ring closure when the naphthalene nucleus was substituted with methyl groups at the positions: 2-, 2,3-, 2,6-, 2,7-, or with a 2-methoxyl group. Since the naming of these compounds and of certain others which contain the same carbon skeleton presents some difficulties, we should like to suggest the name "pleiadene" for the hypothetical parent hydrocarbon, IX.[9]



IX



X



XI

The pleiadones, as we may call the 7-ring ketones, present no special points of interest. The carbonyl group is accessible to the Grignard re-

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[8] L. F. Fieser and Mary A. Peters (now Mary Peters Fieser), THIS JOURNAL, **54**, 3742 (1932).

[9] 1,8-*o*-Xylylenenaphthalene thus becomes "7,12-dihydro-pleiadene." The possibility of dehydrogenating this compound and of obtaining the truly aromatic, anthracene-like hydrocarbon, IX, is under investigation.

action, but not to condensation with hydroxylamine in an alcoholic alkaline medium. The methylated ketones were all convertible in excellent yield into the corresponding diketones. The oxidation of 1-methoxy-7-pleiadone, X, was also successful, if somewhat less smooth. The product (XI), whose structure obviously is fixed by this synthesis, proved to be identical with the methyl ether[10] of phthaloylnaphthol. Rieche's formula is thus confirmed by the present synthesis.

We can as yet offer no interpretation of the oxidation of phthaloylnaphthol, a reaction which appears to involve a reduction of one of the carbonyl groups. Rieche's suggestion of the intermediate formation of a radical is of little help here and, as applied to the formation of the second oxidation product isolated by Rieche, namely, hydroxybenzanthrone, it is inadmissible, for the hydrogen atom which he considers eliminated in the first phase of the reaction must appear in the final product. The search for intermediate oxidation products offers the most promising method of attacking the problem further, but since Rieche has already indicated that he is engaged in such a study, further work on our part in this direction has been abandoned for the present. Our studies thus have been directed into other channels, and we may report at this time the discovery of interesting reaction products of phthalylnaphthol with hydroxylamine and with diazomethane. These results, which lead to a new view of the fine structure of the compound in question, will be offered soon for publication.

Experimental Part[11]

1. The Structure of the Oxidation Product

An improved yield (75.6%) of benzhydrol-2,3,2'-tricarboxylic acid lactone (II) resulted from the use of phthaloylnaphthol which had been distilled and crystallized from glacial acetic acid, and in working up the mother liquor from the manganese salt.[4] One further derivative briefly examined was the *imide*, prepared by heating the anhydride of the acid with concentrated ammonia solution. It formed colorless needles melting at 303–304° from glacial acetic acid.

Anal. Calcd. for $C_{16}H_9O_4N$: C, 68.81; H, 3.25. Found: C, 68.68; H, 3.28.

The titrations of the acid previously reported[4] were made with barium hydroxide in aqueous medium and they revealed only the presence of the two free carboxyl groups. On using alcoholic potassium hydroxide solution (0.036 *N*) and an alcoholic solution of the acid, we found again a sharp end-point corresponding to the two free carboxyl groups. Alkali added beyond this point was only consumed after the solution had been boiled for several minutes, but the amount eventually taken up was nearly equal to that calculated for a third, masked carboxyl group. Thus 0.1844 g. of acid required 34.3 cc. of reagent for the first end-point (calcd., 34.4 cc.) and 16.5 cc. for the second (calcd., 17.2 cc.). The behavior was entirely similar to that of the known benzhydrol-2,2'-dicarboxylic acid lactone.

Diphenylmethane-1,1,2'-tricarboxylic Acid, IV.—The reduction of the tricarboxylic acid lactone, II, by the action of fused alkali proceeds smoothly and gives a very pure product, but the yields are never high, probably because the reaction is one of dispro-

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[10] Knapp, *Monatsh.*, **60**, 189 (1932).

[11] For the analyses here reported we are greatly indebted to Dr. C. Harold Fisher

portionation. The addition of potassium formate gave a slightly cleaner product without materially increasing the yield.

To a melt of 60 g. of potassium hydroxide heated at about 180°, 10 g. of the lactone was added in small portions with good stirring. It at first formed a yellow gum and then dissolved to a clear, reddish-yellow melt. After heating for a few minutes up to the point at which boiling took place, the melt was cooled and dissolved in 200 cc. of water. The product was first separated in the form of its mono-potassium salt by adding hydrochloric acid until there was no further increase in the amount of the precipitate which separated even from a hot solution. The salt was suspended in 100 cc. of hot water, brought into solution by the addition of hydrochloric acid, and on cooling the diphenylmethanetricarboxylic acid separated in a crystalline and practically pure condition; yield 3.5-4.2 g.

The acid is insoluble in hydrocarbon solvents and very soluble in water. From the latter solvent it separated in the form of colorless needles of a hydrate. When heated at the ordinary rate, this is observed to lose water and melt at about 145°, to solidify and to remelt at about 200° (the anhydride). The material cannot be dried thoroughly without some anhydride formation. Samples dried at room temperature gave the following analytical results:

Anal. Calcd. for $C_{16}H_{12}O_6 \cdot 1.5H_2O$: C, 58.71; H, 4.62. Found: C, 58.81, 59.05; H, 4.66, 4.66. Titrated with 0.036 *N* alcoholic potassium hydroxide solution, 0.1746 g. required 43.4 cc., while the quantity calculated on the basis of the above formula and the assumption of three carboxyl groups is 44.4 cc.

The trimethyl ester was prepared by the use of diazomethane and purified by distillation and crystallization from dilute methyl alcohol. It formed colorless prisms melting at 79°.

Anal. Calcd. for $C_{19}H_{18}O_6$: C, 66.65; H, 5.30. Found: C, 66.53; H, 5.31.

The anhydride was easily obtained by distillation of the acid in vacuum. It crystallized well from xylene as excellent, stout needles melting at 202°. It dissolves in cold soda solution.

Anal. Calcd. for $C_{16}H_{10}O_5$: C, 68.07; H, 3.57. Found: C, 67.98; H, 3.54.

Anthrone (Anthranol)-1,5-dicarboxylic Acid (V) and Anthraquinone-1,5-dicarboxylic Acid.—Triphenylmethane-1,2,1′-tricarboxylic acid dissolves in concentrated sulfuric acid without the development of much color, but when the solution (1 g. in 10 cc.) was heated at 150° for five minutes it assumed a deep green color. The rust-colored product which was precipitated with water appeared to be a mixture of the anthrone and the anthraquinone. It was converted into a pure sample of the quinone by the method employed by Scholl: digestion with boiling, concentrated nitric acid and precipitation from a solution in ammonia. It was thus obtained as fine yellow needles melting with decomposition at 399° (Scholl: above 390°).

Anal. Calcd. for $C_{16}H_8O_6$: C, 64.86; H, 2.72. Found: C, 64.58; H, 2.78.

The substance corresponded in every way with the description given by Scholl and his collaborators.[12] To make certain of the identity, we prepared the mixed anhydride with acetic acid, m. p. 208°, with decomposition (S., about 202°); the acid **chloride**, m. p. 264–265° (S., 260–263°); the dimethyl ester, m. p. 239° (S., 236°); and the hydroquinone dilactone (decomposes). The dilactone was conveniently prepared by boiling the quinone with acetic anhydride to give a solution of the mixed anhydride, and adding zinc dust and sodium acetate; red crystals of the dilactone were soon deposited from the boiling solution. All of the compounds here mentioned responded to the various tests given by Scholl.

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[12] Scholl and co-workers, *Ber.*, **62**, 107, 616, 1424 (1929).

To obtain the anthrone dicarboxylic acid without any subsequent oxidation, the anhydride of diphenylmethane tricarboxylic acid (5 g.) was heated at 150° for fifteen minutes in a melt from 12.5 g. of sodium chloride and 62.5 g. of aluminum chloride. On pouring the melt onto ice and purifying the precipitate by dissolution in soda solution there was obtained 4.6 g. of a clean, orange-red powder. This corresponded well with the description given by Scholl and Böttger,[7] and this was also true of the lactone and its mixed anhydride prepared from the acid. Since the compound does not crystallize well, and since none of the derivatives have characteristic melting points, our identification of the anthrone rests upon the identification given above of the corresponding quinone. The latter could be obtained in quantitative yield by boiling the anthrone with concentrated nitric acid.

2. Derivatives of 1′-Naphthylmethyl-2-benzoic Acid

The naphthoyl-2-benzoic acids required for the synthesis of the pleiadones have all been described.[4,8] The preparation of 2-(2′-methoxy-naphthoyl-1′)-benzoic acid, m. p. 196°, was considerably improved by carrying out the Friedel and Crafts reaction at −15 to 0°. Two to three days must be allowed for the condensation, but no hydrolysis of the ether group occurs under these conditions. The acid is best crystallized from alcohol.

The reduction of the keto acids was accomplished by the action of zinc dust in an alkaline solution; for 10 g. of acid we used 15 g. of sodium hydroxide, 200 cc. of water and 30 g. of zinc dust. When working with large quantities the mixture should be heated on the steam-bath for at least two days, or else boiled for a somewhat shorter time. Otherwise the reduction may be incomplete and the product contaminated with the lactone of the intermediate carbinol. Thus in a reduction of 70 g. of the methoxy compound (196°), which was continued for only twenty hours on the steam-bath, there was separated, through its insolubility in soda solution, 13 g. of **the lactone of (2′-methoxy-1′-naphthyl)-(2-carboxyphenyl)-carbinol,** which formed large, colorless prisms from alcohol, m. p. 139°.

Anal. Calcd. for $C_{19}H_{14}O_3$: C, 78.60; H, 4.86. Found: C, 78.21; H, 5.25.

The new acids prepared are listed in Table I. The acids usually separate on acidifying an alkaline solution in a hydrated condition and it is well to digest the precipitate at the boiling point, when the mass coagulates, melts, and slowly changes to a granular solid. The best solvent for crystallization is a benzene–ligroin mixture. The yield of pure material was usually of the order of 70–80%.

TABLE I

DIMETHYL-1′-NAPHTHYLMETHYL-2-BENZOIC ACIDS

Positions of substituents	M. p., °C.	Description	Analyses, %	
			C Calcd.: 82.72	H Calcd.: 6.25
2′, 3′	254	Plates	82.55	6.41
2′, 6′	218	Micro crystals	82.87	6.53
2′, 7′	211	Fine needles	82.76	6.72

3. The Pleiadones

The acids used in the preparation of the 7-ring ketones of type VIII were those listed in Table I, 2′-methyl-1′-naphthylmethyl-2-benzoic acid[8] and the 2′-methoxy acid.[13] Cyclization with sulfuric acid was tried in two cases, but the results were not promising and the following general method was used. Ten grams of the acid, which should be quite pure and in a finely divided condition, was warmed gently with 15 cc.

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[13] This acid, m. p. 196°, was incorrectly called 2-(2′-methoxynaphthyl-1′)-benzoic acid, in the previous paper, Ref. 4.

of purified thionyl chloride until the material was all dissolved. The thionyl chloride was taken off at the pump with gentle heating (60–70°), and the residue was dissolved in dry ether and again evaporated at reduced pressure. The acid chloride usually was obtained at this point as a clean, hard solid. It was taken up in about 100 cc. of nitrobenzene, and the solution was cooled in an ice-bath and treated with 8 g. of aluminum chloride. The solution soon acquired a deep red or claret color of great beauty, and in some cases an addition product separated out. The flask was shaken intermittently for two hours and left in the ice-bath for at least ten hours. On adding ice water and removing the solvent with steam, the ketone was left as a more or less hard, slightly brown solid. The method most suitable for purification depends upon the character of the crude product. Distillation in vacuum is advantageous in any case, but unless the material can be thoroughly dried it is advisable to crystallize it once from glacial acetic acid or alcohol before the distillation. The yield of pure product usually ranged from 75 to 85%, though in working with quantities no larger than that given the yield was often considerably higher.

The properties and analyses of the new ketones synthesized, and of two derivatives of the first one, are summarized in Table II. They are all nicely crystalline compounds. The methylated derivatives are all very soluble in benzene and are best crystallized from alcohol, glacial acetic acid or ligroin. The faint color noted in two cases may be due to slight traces of impurities, for the compounds described as colorless were not easily obtained in this condition. We attempted to decolorize the 1,2-dimethyl derivative by shaking a benzene solution with sulfuric acid, but the ketone was extracted into the acid in the form of a bright red halochromic salt and the recovered material was still yellow. The 1-methyl derivative was first obtained in a colorless condition when it was boiled for several hours in a solution of alcoholic alkali containing hydroxylamine. The only result was the removal of a trace of color.

TABLE II

DERIVATIVES OF 7-PLEIADONE

Positions of substituents	M. p., °C.	Description	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
1-Methoxy	160	Yellow prisms	83.18	83.30	5.15	5.28
1-Hydroxy	232	Bright yellow needles	83.05	82.82	4.65	4.66
1-Acetoxy	195	Pale yellow needles	79.45	79.23	4.67	5.10
1-Methyl	128	Colorless needles	88.34	88.23	5.46	5.31
1,2-Dimethyl	192	Pale yellow needles	88.20	87.89	5.93	5.97
1,5-Dimethyl	159	Pale yellow prisms	88.20	87.84	5.93	5.95
1,6-Dimethyl	172	Colorless needles	88.20	88.08	5.93	6.11

1-Hydroxy-7-pleiadone was prepared by boiling a solution of 5 g. of the methyl ether in benzene with 15 g. of aluminum chloride for five hours. After adding ice and removing the solvent by steam distillation, the product was precipitated from an alkaline solution and digested at the boiling point. This gave in quantitative yield a clean, bright yellow product. It forms very good crystals from alcohol, in which it is readily soluble. The substance dissolves easily in cold alkali to give a deep orange solution from which an orange salt separates on adding more alkali. The solution in concentrated sulfuric acid is bright red. The compound was recovered unchanged after being heated for several hours in a strongly alkaline solution with hydroxylamine. The deep color of the alkaline solution is discharged by heating with zinc dust for a short time, but no good product was isolated from the resulting pale yellow solution.

A Grignard reaction product, probably **1-methoxy-7-hydroxy-7-phenyl-7,12-dihydropleiadene**, was obtained from the 1-methoxy compound and phenylmagnesium bromide. The product, which was prepared only on a small scale, formed clusters of colorless needles from glacial acetic acid; m. p. 186°. It formed no acetate with acetic anhydride and sodium acetate, and it could be distilled in vacuum without decomposition.

Anal. Calcd. for $C_{25}H_{20}O_2$: C, 85.18; H, 5.72. Found: C, 84.77; H, 5.30.

1-Methyl-7-pleiadone gave a different type of product in the reaction with phenylmagnesium bromide. The compound obtained forms faintly yellow needles from glacial acetic acid, m. p. 237°, and has the composition of *a hydrocarbon;* found: C, 93.83; H, 5.83.

4. The Pleiadenediones (Phthaloylnaphthalenes)

The conversion of the ketones to diketones was accomplished by boiling a solution of 1 g. of material and 1.6 g. of sodium dichromate in glacial acetic acid for two and one-half hours. Except in the case of the methoxy compound, the product which precipitated on pouring the green solution into water was obtained in a pure condition after digestion with soda solution and crystallizing once from glacial acetic acid. The yield usually was about 90% of the theoretical amount. The analyses of the compounds are recorded in Table III. The 1-methyl derivative is the most soluble member of the series, the high-melting 1,6-derivative is the least so. Thus the former crystallizes well from alcohol, the latter is only sparingly soluble in this solvent.

TABLE III

DERIVATIVES OF 7,12-PLEIADENEDIONE

Positions of substituents	M. p., °C.	Description	Carbon, %		Hydrogen, %	
			Calcd.	Found	Calcd.	Found
1-Methyl	183	Faintly yellow needles	83.80	83.76	4.45	4.40
1,2-Dimethyl	175	Faintly yellow needles	83.89	83.41	4.93	4.75
1,5-Dimethyl	179	Pale yellow needles	83.89	83.62	4.93	4.93
1,6-Dimethyl	241	Colorless plates	83.89	83.34	4.93	4.80

The crude oxidation product obtained from methoxypleiadone was more difficult to purify. It was digested with soda solution, crystallized once from glacial acetic acid, distilled, and crystallized repeatedly from the same solvent; yield, about 10%. The best sample gave well formed, yellow prisms melting at 204°. The methyl ether of phthaloylnaphthol, prepared with the use of dimethyl sulfate according to Knapp,[10] melted at 205° and the mixture of the samples melted at 204–205°. Attempts to oxidize the acetate of hydroxypleiadone were unsuccessful.

In none of the previous work on phthaloylnaphthol has there been any direct demonstration of the presence of two carbonyl groups. The quantitative test with the Grignard reagent reveals only one active hydrogen and one carbonyl group.[4] Tested in the same way, the above methyl ether gave no gas but consumed exactly two moles of reagent. The only Grignard reaction product examined was that obtained from 1-methylpleiadenedione and phenylmagnesium bromide. The substance appears, however, to contain two hydrogen atoms less than would be expected for addition at both carbonyl groups. The *compound* formed clusters of slightly yellow needles, m. p. 183–184°, from glacial acetic acid.

Anal. Calcd. for $C_{31}H_{22}O_2$: C, 87.29; H, 5.21. Found: C, 87.32; H, 4.83.

The analysis of the *acetate*, colorless needles from alcohol, m. p. 212°, serves to confirm this formulation.

Anal. Calcd. for $C_{33}H_{24}O_3$: C, 84.58; H, 5.16. Found: C, 84.39; H, 4.91.

One fact of significance about the five diketones described above is that in every case the solubility in alcohol is markedly increased by the addition of alkali. This is most clearly seen by chilling suddenly a hot, saturated solution of one of the compounds in alcohol, and then adding a small quantity of sodium hydroxide solution. On shaking in the cold, the solid soon dissolves. It separates again on diluting the solution with water or on neutralizing with glacial acetic acid. A similar solubility of phthaloylnaphthalene was noted first by one of us[4] and later by Rieche.[5] A theoretical interpretation of the phenomenon will be presented in a later paper.

Summary

A product previously obtained by the oxidation of 1,8-phthaloyl-2-naphthol has been reëxamined and the structure originally assigned has been confirmed. Since it is difficult to account for the formation of this oxidation product on the basis of the structure indicated for the starting material, a new and reliable synthesis was developed. This synthesis establishes the correctness of the formula, and, at the same time, affords a general method of obtaining derivatives of an interesting type of aromatic hydrocarbon for which we have suggested the name "pleiadene."

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Studies in the Ketone Sugar Series. III. Open-Chain Derivatives of Fructose and Turanose*

BY EUGENE PACSU AND FRANK V. RICH

In Part I[1] of this series it has been shown that on direct acetylation of turanose by acetic anhydride in the presence of zinc chloride at room temperature, three octaacetates are obtained. One of these behaves in many respects differently from the other two and also from the fourth octaacetate obtained from the stable bromoacetylturanose. A colorless acetone solution of this isomer, described in Part I as "the third octaacetate," becomes yellow on the addition of a few drops of dilute sodium hydroxide solution. After neutralization with dilute sulfuric acid, the color disappears and the solution will reduce potassium permanganate solution. None of the other known octaacetates shows such behavior when submitted to the same test. Furthermore, this same octaacetylturanose can be recovered unchanged after treatment with hydrogen bromide dissolved in glacial acetic acid. This observation led to the assumption that the octaacetate contains no active acetoxyl group and that it is a derivative of the open-chain fructose with a free ketone group. It was found that this compound could be prepared from β-heptaacetylturanose by acetylating with acetic anhydride and zinc chloride. In Part II[2] it has been shown that the β-heptaacetate very probably contains an "ortho-ester" structure. Since

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* The conclusions referring to the fructose derivatives have already been reported [Pacsu and Rich, THIS JOURNAL, **54**, 1697 (1932)].

(1) Pacsu, THIS JOURNAL, **54**, 3649 (1932).

(2) Pacsu, *ibid.*, **55**, 2451 (1933).