peatedly washed with ether and alcohol, to remove any unconverted pyrazolone and benzaldehyde, dried and analyzed.

Calculated for $C_{14}H_{10}N_2O_2$, N, 11.75. Found, 11.47.

This compound is insoluble in most organic solvents. By heating with nitrobenzene or acetophenone, some of it dissolves, giving a red solution, but on cooling only a very small amount separates out. It does not melt at 300°. Heated with sodium hydroxide solution, it gives the odor of benzaldehyde. Concentrated sulphuric acid dissolves it, giving a red solution.

Work upon ethyl pyromucylacetate and its pyrazolone derivatives will be continued in this laboratory.

THE CONSTITUTION OF 1-PHENYL-2,3-NAPHTHALENE-DICARBOXYLIC ACID.

BY JOHN E. BUCHER.

Received June 8, 1908.

About ten years ago Michael and Bucher[1] obtained the anhydride of the above acid by the action of acetic anhydride on phenylpropiolic acid. They made a thorough study of the compound and were finally able to give conclusive proof of the correctness of the above constitution. The compound has since been obtained by a number of investigators who were evidently not aware of this work.

Lanser[2] obtained the anhydride by the action of phosphorus oxychloride on phenylpropiolic acid. He did not determine the molecular weight of the product but he described the compound as the anhydride of triphenyltrimesic acid. The formula of this compound would be $C_{54}H_{30}O_9$, corresponding to a molecular weight of 822. Michael and Bucher had shown that their compound has the composition $C_{18}H_{10}O_3$ and the molecular weight of 274.

Manthey[3] then made the compound according to Lanser's method, proving that the formula is $C_{18}H_{10}O_3$ by determining the molecular weight of its methyl ester. In addition, he showed that the anhydride is the derivative of a dibasic acid by measuring the electrical conductivity of the sodium salt. The carboxyl groups were also shown to be in the ortho position. From these facts he concluded that the acid is diphenyltetrendicarboxylic acid. These facts are not sufficient for the determination of the constitution of the compound as the following formulae show:

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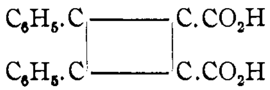
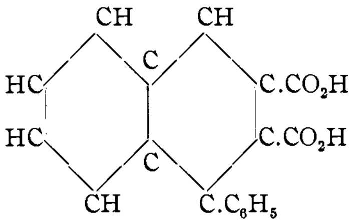
[1] *Am. Chem. J.*, **20**, 89 (1898).

[2] *Ber.*, **32**, 2478 (1899).

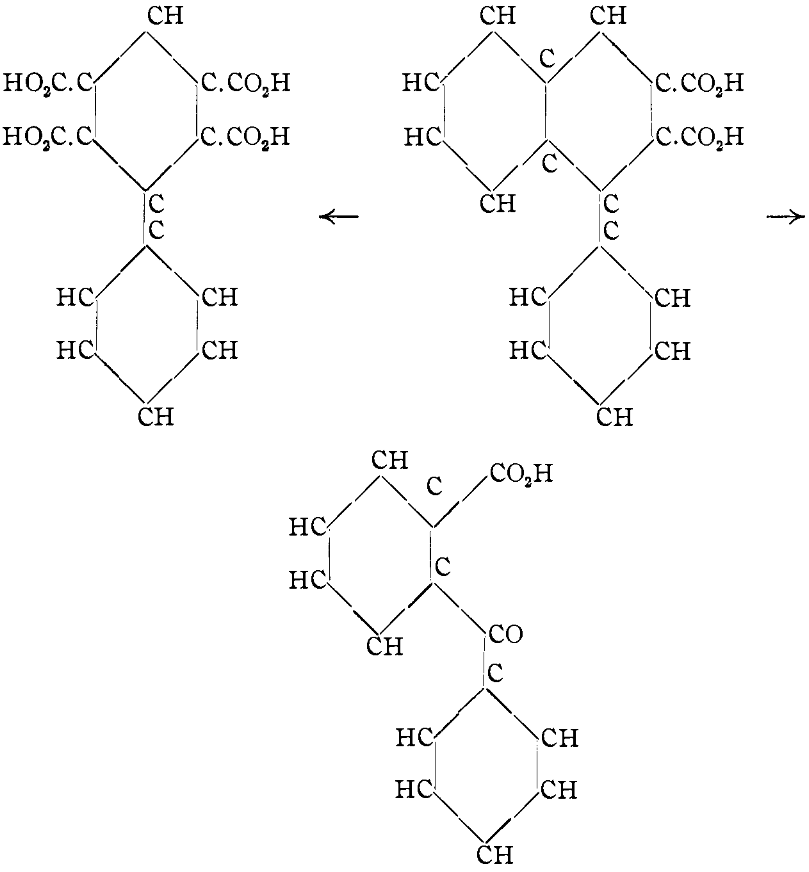
[3] *Ibid.*, **33**, 3083 (1900).





Both acids would have the carboxyl groups in the ortho position and the composition of the corresponding anhydride would be $C_{18}H_{10}O_3$.

Lanser and Halvorsen[1] later acknowledge the correctness of Manthey's work and accept his view that the acid is a tetren-derivative. These investigators prepared a number of derivatives such as acid esters, imids and the fluorescein of the acid. These compounds would correspond equally well to the naphthalene constitution for the acid.



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[1] *Ber.*, 35, 1407 (1902).

Ruhemann and Meriman[1] also obtained the compound but did not investigate its constitution.

At this point, Michael[2] prepared the compound by Lanser's method and showed that it is identical with the 1-phenylnaphthalene-2,3-dicarboxylic anhydride obtained by Michael and Bucher. The latter investigators proved the constitution of their product by oxidizing it to diphenyltetracarboxylic acid in alkaline solution and to *o*-benzoylbenzoic acid in acid solution. These relations are shown by the above formulae. They also prepared the corresponding hydrocarbon, identifying it by the physical properties and by oxidizing it to *o*-benzoylbenzoic acid. These reactions show with certainty that the acid is a naphthalene derivative and they cannot be reconciled with the view that the compound is a diphenyltetrendicarboxylic acid.

Recently, Stobbe[3] obtained the above anhydride by the action of light on dibenzalsuccinic acid and examined its properties. In this paper he entirely misrepresents the work of Michael and Bucher. A brief general reply[4] has been made to this article. On repeating the greater part of Stobbe's work, I have found parts of it to be incorrect. The publication of some of my results has also been anticipated. Under these circumstances, I feel that it is necessary for me to make this further reply to Stobbe's work and to give an account of the results already obtained.

Stobbe claims to have been the first to observe the formation of *o*-benzoylbenzoic acid by the direct oxidation of the anhydride and therefore to have given the first proof that the compound is a naphthalene derivative. He says this formula "wird erst gestützt durch die zuerst von uns beobachtete Tatsache, dass die Säure oder besser ihr Anhydrid bei der Oxydation mit Chromsäure unter Starker Kohlensäureentwicklung *o*-benzoylbenzoesäure liefert." Michael and Bucher[5] obtained this acid ten years ago by the same process. They state "we also made an experiment to oxidize the anhydride directly with chromic anhydride, and were able to isolate benzoylbenzoic acid from the products of oxidation." I have also obtained this acid many times during the past ten years by the direct oxidation of the anhydride. Stobbe's claim of priority is therefore not justified and if this reaction is sufficient proof, it would follow that Michael and Bucher showed the constitution of the compound in their original paper.

Stobbe also oxidized the compound in alkaline solution with potassium

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[1] *J. Chem. Soc.*, **87**, 1389 (1905).

[2] *Ber.*, **39**, 1908 (1906).

[3] *Ibid.*, **40**, 3372 (1907).

[4] *Ibid.*, **41**, 70 (1908).

[5] Michael and Bucher, *Am. Chem. J.*, **20**, 112 (1898).

permanganate, obtaining results differing from those of Michael and Bucher. He states that he kept his experimental conditions similar to theirs! In their original paper the experiments were carried out by using more than 5 *parts* of potassium permanganate for one part of the acid and in one case the solution was *boiled for four hours.* On the other hand Stobbe used only 2.5 *parts* of potassium permanganate to one part of the acid and he *cooled the solution with ice.* These conditions are entirely different and no doubt explain Stobbe's failure to get diphenyltetracarboxylic acid. He says "Wir dagegen haben selbst bei sehr vorsichtiger Oxydation immer nur harzige Säuren, Oxalsäure, Benzoesäure, ein einziges Mal eine hochmolekulare, in Wasser verhältnismässig leicht lösliche Säure (Schmp. 200°) und einmal sogar Benzaldehyd erhalten; die eben eswähnte Diphenyltetracarbonsäure, Phthalsäure, *o*-Benzoylbenzoesäure, auch Benzil wurden von uns nie beobachtet. Hieraus folgt, dass die Phenylnaphthalindicarbonsäure leicht tiefergehende zersetzungen erleidet, und dass deshalb diese Reaktion wenig zur Aufklärung ihrer Konstitution beitragen kann." Stobbe's error in this case is due to not following the original directions. His "sehr vorsichtiger Oxydation" is really *incomplete oxidation* and it accounts for the "harzige" acids he obtains. These acids instead of being due to "tiefergehende zersetzungen" are mostly *intermediate products* between the original acid and the diphenyltetracarboxylic acid. This is shown by the fact that I obtained over 200 grams of this acid by oxidizing more strongly some such intermediate residues, which had accumulated in this laboratory. This oxidation when properly conducted yields products which are unusually free from resinous substances and is therefore particularly well adapted for determining the constitution of the anhydride. Not only is the diphenyltetracarboxylic acid formed in this process but very appreciable quantities of *o*-benzoylbenzoic acid are also formed.

As Stobbe has taken up this work, it may be well to give a summary of my work on the oxidation at this point. If 50 grams of 1-phenylnaphthalenedicarboxylic acid are taken up in hot caustic alkali solution and oxidized with 150 grams of potassium permanganate in boiling solution until the color of the permanganate disappears, the products will be about as follows after separating with barium hydroxide; 6 grams of diphenyltetracarboxylic acid, 40 grams barium salt of 1-phenyl-phenyl-*o*-glyoxyl-3,5,6-tricarboxylic acid, 45 grams barium salt of 1-phenyl-phenyl-*m*-glyoxyl-2,5,6-tricarboxylic acid, 1.5 grams ammonium salt of *o*-benzoylbenzoic acid and about 3 grams of acids of unknown constitution which are very soluble in a *small* quantity of water but separate partially on further dilution with water and form very soluble barium salts. Under these conditions, small quantities of oxalic acid were also obtained but no benzoic acid was found although traces may have been present. The fact that only about 6 grams of the diphenyltetracarboxylic acid but a large quantity (85 grams of barium salts) of the above two intermediate ketonic acids were obtained by this energetic oxidation shows how incompletely Stobbe oxidized the acid. Many experiments were tried, using from 1.5 to 6 parts of potassium permanganate to one part of acid and varying the conditions from cooling with ice to boiling the solution. In *all cases*, *diphenyltetracarboxylic acid* and the two intermediate ketonic acids were obtained. On oxidizing the acid with *six* parts of permanganate in boiling solution, a yield of 15 grams of diphenyltetracarboxylic acid was obtained from 50 grams. In this case the energetic oxidation destroyed the oxalic- and *o*-benzoylbenzoic acids but a small quantity of benzoic acid was found while the final residue of acids of unknown constitution was small. On oxidizing in the cold with about 2.5 parts of permanganate, the quantity of partially oxidized products is increased and, in addition, a new acid was isolated. This acid is an intermediate product, since it can easily be oxidized to diphenyltetracarboxylic acid. It yields much hydrogen on fusion with caustic alkali. It melts at 195–205° with decomposition. Titration of the acid with potassium hydroxide and the analysis of its silver salt indicate a molecular weight of 388 or 390.

Analysis: 0.1933 gram substance gave 0.3937 gram CO_2 and 0.0632 gram H_2O.

	Calculated for			
	$C_{18}H_{12}O_{10}$.	$C_{18}H_{13}O_{10}$.	$C_{18}H_{14}O_{10}$.	Found.
C	55.68	55.54	55.40	55.54
H	3.12	3.38	3.64	3.63

These compounds differ so slightly in composition that it is practically impossible to distinguish them by analysis. It is very probable, however, that the acid has the composition $C_{18}H_{12}O_{10}$ or $C_{18}H_{14}O_{10}$ and it is derived by water splitting out from a hydroxy acid. This acid is now being studied with the hope of determining its constitution.

I have never noticed the odor of benzoic aldehyde when oxidizing *pure* 1-phenylnaphthalenedicarboxylic acid, but have noticed it occasionally when working with impure products. Also, under no condition in the experiments were any considerable quantities of benzoic acid obtained although some of my experiments had been made under conditions fairly similar to those of Stobbe, who found as much as 60 per cent. of this acid. It scarcely seems possible that a slight variation in the conditions should cause the molecule to break up in such a different way.

Separation of the Oxidation Acids.—The barium salts of these acids have a remarkable combination of properties which I have used for separating the acids during the past four years. The following example will illustrate the principles of the method, when 50 grams of the acid are oxidized with 150 grams of potassium permanganate in boiling solution. After filtering, concentrating and acidifying, the acids are extracted with ether. After distilling the ether on the water-bath, a viscous product which swells up very much *in vacuo* is obtained. The last traces of ether are removed by adding about an equal weight of water and boiling the solution at 15 mm. until the odor of the ether disappears. On standing, some pure diphenyltetracarboxylic acid usually crystallizes from the viscous solution. This is filtered off at the suction pump. After adding a few drops of phenolphthalein solution, the filtrate is neutralized with a cold solution of barium hydroxide, so that the final volume is about 2500 cc. Any flocculent precipitate which may form is filtered off *quickly*. This precipitate is usually so small that it may be rejected. After standing for about an hour, clear crystals appearing like rhombohedrons will be noticed adhering to the walls of the glass. The separation of this salt can be hastened by thorough stirring with a glass rod, or the solution may be allowed to stand over night. This salt, containing the main fraction of the 1-phenyl-phenyl-*o*-glyoxyl-3,5,6-tricarboxylic acid is filtered off. The filtrate is then boiled for a few minutes. *Near the boiling point*, the solution becomes turbid from the separation of the barium salt of the diphenyltetracarboxylic acid. Since this barium salt is almost insoluble in water,[1] this affects practically a quantitative separation of the acid at this point. The hot filtrate is concentrated on the water-bath to a total weight of about 200 grams and allowed to stand for several hours. This causes the separation of the second crop of rhombohedral-like crystals of the barium salt of 1-phenyl-phenyl-*o*-glyoxyl-3,5,6-tricarboxylic acid. As this salt is very sparingly soluble in water this causes nearly complete removal of this acid. The filtrate is concentrated in a *tall narrow* beaker, placed in a water-bath until it becomes a thick paste. The salt which has separated is filtered off at the suction pump and washed cautiously with warm water. The filtrate is concentrated once or twice after this to recover the remaining portions of this salt. This is the barium salt of 1-phenyl-phenyl-*m*-glyoxyl-2,5,6-tricarboxylic acid, and it can be separated quite closely in spite of the fact that it is much more soluble than the salts of the two preceding acids. The barium salts now remaining in the mother liquor are very soluble, a thick sirup being obtained on concentration. The acids were therefore recovered from this solution by acidifying with hydrochloric acid and extraction with ether. The viscous acid residue was made alkaline with concentrated ammonia. This caused the immediate separation of the sparingly soluble ammonium salt of *o*-benzoylbenzoic acid. The filtrate from the ammonium salt of the *o*-benzoylbenzoic acid contained only a few grams of acids which could not be separated or identified.

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[1] *Am. Chem. J.*, **20**, 104 (1898).

These acids on further oxidation with potassium permanganate yield additional quantities of the diphenyltetracarboxylic acid and the ketone acids, thus showing that, in part, they consist of incompletely oxidized material.

The properties of the barium salts upon which the above separation is based are as follows:

(1) The barium salt of diphenyltetracarboxylic acid shows no tendency to separate from even moderately concentrated solutions of the pure salt on standing for several weeks. In the actual separation it is well to have the solution rather dilute and not to allow it to stand longer than necessary, as the salts of some other acids may cause it to precipitate. The salt precipitates *very* completely on boiling the solution and does not redissolve to any noticeable extent on cooling the solution.

(2) The barium salt of 1-phenyl-phenyl-*o*-glyoxylic-3,5,6-tricarboxylic acid begins to separate from its strong solutions in less than a minute and the crystallization is soon complete. At the dilution used in these experiments there was very little separation even at the end of an hour unless the solution was seeded with crystals of the salt and stirred vigorously. Boiling the solution may start the crystallization of the salt. It is therefore necessary to remove the greater portion of the substance at the ordinary temperature. Otherwise a portion of this salt would precipitate with that of the diphenyltetracarboxylic acid. The second fraction of this salt is then separated by concentrating the filtrate.

(3) The barium salt of the diphenyl-phenyl-*m*-glyoxylic-2,5,6-tricarboxylic acid separates from the hot solution only after considerable concentration but when it has once separated it *does not redissolve readily*, even in hot water. It can therefore be removed quite completely.

(4) The barium salts of the residual acids are all very soluble and do not interfere with the separation of the three principal acids.

With slight modifications which will be published in a later paper, this method works equally well in the presence of some additional acids which are formed under other conditions of oxidation.

The above ketone acids are very stable toward potassium permanganate in alkaline solution but they are *oxidized immediately in acid solution.* This reaction has proved of great service in studying a large number of ketone acids which we now have on hand. This was found true for all of our acids and the literature of such ketonic acids indicates that these properties are general. These facts suggest the following method of oxidation, if diphenyltetracarboxylic is desired rather than the two intermediate ketonic acids. The acid is oxidized with 2.5 parts of potassium permanganate in boiling alkaline solution. After removing the oxides of manganese, the solution is concentrated and then strongly acidified with sulphuric acid. A saturated solution of potassium permanganate is then allowed to flow into the slightly warm solution from a burette. The color disappears at once until the oxidation is complete. At this point the oxides of manganese will begin to precipitate, indicating that the oxidation is completed. In this way 3.2 grams of diphenyltetracarboxylic acid were obtained from 5 grams of acid. On oxidizing the remaining acids again in acid solution only 0.1 gram more of diphenyltetracarboxylic acid was obtained. The residue was now oxidized again in alkaline solution followed by oxidizing in acid solution as in the above oxidation. This yielded 0.7 gram more acid, increasing the total yield to 4 grams. This shows that oxidation with 2.5 parts of permanganate is so incomplete that a considerable portion of the products are not even oxidized as far as the ketone acids. A second oxidation in *alkaline* solution then oxidizes these products to the ketone acids and these in turn are finally oxidized to diphenyltetracarboxylic acid in acid solution. These results prove the correctness of the original work of Michael and Bucher and that the action of Stobbe in ignoring the existence of diphenyltetracarboxylic acid is not justifiable.

They also show the nature of the impure intermediate product obtained by Michael and Bucher.[1] This product which they were unable to purify must have consisted largely of a mixture of the two isomeric 1-phenyl-phenyl-*o*-glyoxyl-3,5,6-tricarboxylic and 1-phenyl-phenyl-*m*-glyoxyl-2,5,6-tricarboxylic acids. These two ketone acids can now be separated very easily by means of their barium salts. Analysis shows that their composition is expressed by the formula $C_6H_5.C_6H(CO_2H)_3CO—CO_2H$. Both give a very satisfactory yield of diphenyl for the hydrocarbon. They are very stable toward alkaline potassium permanganate solution but oxidize very easily to diphenyltetracarboxylic acid in acid solution. On fusion with caustic alkali, they yield tribasic acids. They are very easily soluble in water and both resemble phthalonic acid very closely. These reactions show that they are ketone acids. Reduction with hydriodic acid yields a number of products. The acid giving the sparingly soluble barium salts yields a tribasic acid analyzing for the formula $C_{16}H_{10}O_6$ and giving a good yield of *fluorene* for the hydrocarbon. The reduction must have been accompanied by the loss of carbon dioxide and the formation of a *fluorene ring* as shown by the following formulae. This reduction takes place at a comparatively low temperature, showing that the 1-phenyl-phenyl-*o*-glyoxyl-3,5,6-tricarboxylic acid forms the fluorene compound very readily.

The 1-phenyl-phenyl-*m*-glyoxyl-3,5,6-tricarboxylic acid under similar conditions gives an acid corresponding to the structural formula $C_6H_5.C_6HCH_3(CO_2H)_3$. The hydrocarbon from this acid is an oil and it can be oxidized to *m*-phenylbenzoic acid. If the glyoxyl group is re-

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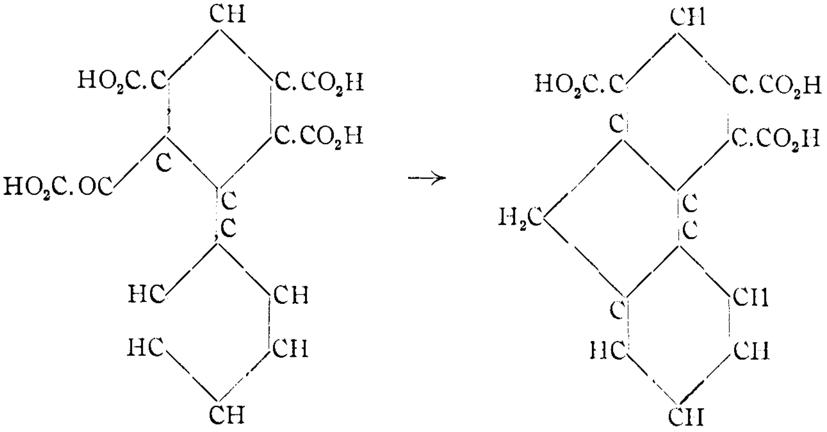
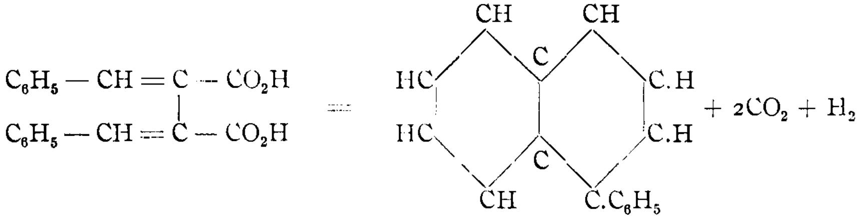
[1] *Am. Chem. J.*, **20**, 107 (1898); *Ber.*, **41**, 71 (1908).



duced with loss of carbon dioxide to the methyl group, the above constitution follows. This evidence justifies the tentative use of the structural formulae given in this paper.

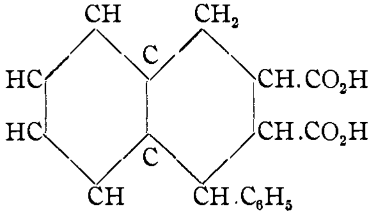
The Hydrocarbon of the Acid.—Stobbe cites among other reactions the formation of 1-phenylnaphthalene from dibenzalsuccinic anhydride in



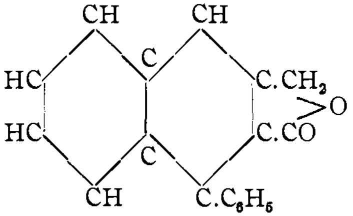
making the hydrocarbons of acids. From this, he concludes that pyrogenic reactions are not suitable for determining constitution, especially in the case of this acid and of 1-phenylnaphthalenedicarboxylic acid. This statement is without justification as the anhydride of dibenzalsuccinic acid even oxidizes (with the loss of two atoms of hydrogen) in benzene solution under the influence of light to the *anhydride of 1-phenylnaphthalenedicarboxylic acid.* It is not surprising that such an acid should also lose hydrogen in making the hydrocarbon by heating with barium hydroxide and in this way form 1-phenylnaphthalene. There is also no reason why this reaction should deceive any one as the hydrocarbon obtained has the composition $C_{16}H_{12}$ while that corresponding to the dibenzalsuccinic acid would be $C_{16}H_{14}$. This fact shows that the reaction can not be used in Stobbe's case but has nothing to do with Michael and Bucher's compound which gives a hydrocarbon having the same number of hydrogen atoms as the acid. This point was considered in making the hydrocarbon. Usually one is not dependent on analysis alone to determine the composition of the hydrocarbon. In all cases I make the hydrocarbon in the preliminary experiments in such a way that the formation of inflammable gases can be noted. This procedure, checked by the analysis should guard against any error of this kind and as the anhydride is very stable there is no reason to suspect any molecular rearrangement. Under the circumstances this reaction, even when considered alone points very strongly to the naphthalene constitution for the substance. However, the direct implication of Stobbe that either Michael or Bucher expressed the view that the formation of this hydrocarbon *alone* affords sufficient proof for the constitution of the anhydride is unreasonable. Why should these investigators after obtaining 1-phenylnaphthalene, diphenyltetracarboxylic acid, *o*-benzoylbenzoic acid, a considerable yield of by-product which was shown to contain acid derivatives of diphenyl, and such negative evidence as the absence of benzil in the oxidation products, only consider the hydrocarbon? In assigning the naphthalene constitution they considered *all* the evidence accumulated during the study of the compound.

That Stobbe's paper is entirely misleading when not compared with the original work is shown by a recent article of Pfeiffer and Möller.[1] They refer to Michael and Bucher's idea of the naphthalene constitution of the compound as "eine Ansicht, die durch eine eingehende Untersuchung von Stobbe ihre Bestätigung erhalten hat." As a matter of fact, Stobbe has added very little new material to the earlier work and has failed to prepare some of the compounds. His proof of the constitution of the anhydride, even if it were original would be much less complete than that given in the first paper of Michael and Bucher.

Reduction of the Anhydride.—Stobbe repeated the reduction of the compound in alkaline solutions with sodium amalgam, confirming the fact that 1-phenyl-1,2,3,4-tetrahydronaphthalenedicarboxylic acid (I) is formed. Michael and Bucher also reduced 5 grams of their anhydride in 50 grams of glacial acetic acid and finally 30 grams of *water* were added. The reduction was affected with 15 grams of zinc dust. In this case they obtained a product which was found to be a lactone. These products can be represented by the following formulae:



I.



II.

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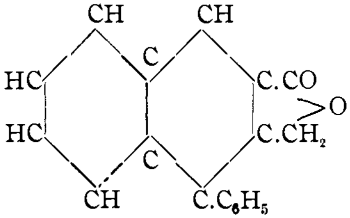
[1] *Ber.*. 40, 3839 (1907).



III.

The lactone obtained would probably correspond to formula II or III. Owing to lack of time this product was not examined thoroughly. Stobbe repeated this work but again failed to follow the conditions. Instead of diluting his acetic acid with from 40 to 60 per cent. of water, he used the glacial acid and added small quantities of dilute *sulphuric acid.* Instead of obtaining *lactone* products he claims to have found 1-phenyl-1,2,3,4-tetrahydronaphthalenedicarboxylic acid (formula I). This supposed difference in product is not due to the difference in preparation. I have repeated Stobbe's experiment and find that it gives the same products as those obtained by Michael and Bucher. In fact, it gives a much better yield of these lactone products than their method, due to the use of *stronger* acetic acid in the reduction. The addition of small quantities of sulphuric acid seems to produce little or no change in the products of the reaction. Not only are lactones formed but *no 1-phenylnaphthalene-1,2,3,4-tetrahydrodicarboxylic acid is formed.* At least, the latter product could not be detected by the very sharp method of separation given below. On reducing 10 grams of anhydride according to Stobbe's directions, about *6 grams of lactones and 3.5 grams of unchanged* 1-phenylnaphthalene-2,3-dicarboxylic anhydride or acid can be isolated from the products. From this it appears that Stobbe's work is entirely incorrect and that lactones are the only new substances formed in any appreciable quantity. His failure is due to the irrational method of separation which he employs and to his relying exclusively on the melting point of 155° to show that his product was the anhydride of the tetrahydro-acid (I) rather than a lactone (II or III). The identification of a supposed compound solely by its melting point in a case involving the rejection of the work of others can not be justified. This is especially true in the present case where an analysis would show 5.3 per cent. difference in the quantity of carbon in the two products. Even dissolving the substances in caustic alkali followed by testing the resulting acids (after they have stood for some time) with sodium carbonate would give conclusive proof of the difference between the anhydride of the acid (I) and the lactones (II or III). This would also give a perfectly sharp method of separating these compounds after the resulting hydroxy acids had again passed into the neutral lactones. Instead of making this sharp separation of acid from neutral products, Stobbe even treated his material with acetyl chloride to convert acids into anhydrides and then relied entirely on crystallization for the separation of these neutral substances. I have found it very difficult if not impossible to separate the lactones even after all acids and anhydrides had been removed. Occasionally a fraction would melt at about 155° on two or three successive crystallizations but on subsequent crystallizations the melting point would rise. Probably this apparently constant melting point accounts for Stobbe's conclusion that he was dealing with the anhydride of the acid (I) rather than the lactones (II or III). Mr. R. C. Weed is now studying these compounds. On crystallizing 14 grams of the lactones from alcohol or acetone many times, he has so far obtained only about 1 gram in the lowest fractions melting at about 135–40° and about 1 gram in the highest fraction melting at 179–81° the greater part of the material remaining in the intermediate fractions. In addition to this mixture, Stobbe's product must also have contained very appreciable quantities of unchanged 1-phenylnaphthalene-2,3-dicarboxylic anhydride which further complicated the separation.

I determined the molecular weight of the 135–40° melting fraction, which corresponds to the substance analyzed by Michael and Bucher. The values found in boiling acetone solution were between 250 and 300. This substance reduces easily in hydriodic acid solution, yielding a monobasic acid which titrates with potassium hydroxides solution for a molecular weight of 261. This corresponds closely with the theory of 260 for a methyl-phenylnaphthalenecarboxylic acid. The substance dissolves easily in dilute caustic alkali on heating. Acids precipitate a pasty acid from this solution. This acid product passes into the neutral lactone again on standing under the mother liquor. These facts show the correctness of the formula assigned by Michael and Bucher. They were not able to obtain a sharper melting point than 135–37° in their purest fraction owing to the difficulty of separating this product from the other neutral material. The entirely pure product would probably melt higher. This particular fraction makes up the smaller part of the neutral product. The larger fractions of higher melting substance also show a molecular weight corresponding to the formula $C_{18}H_{12}O_2$ and their conduct toward alkalies is exactly like that of the lowest melting substance. These fractions do not yield a corresponding monobasic acid on reducing with hydriodic acid under the same conditions as used in the above case. These experiments make it rather probable that the entire neutral product is made up of the two isomeric lactones represented by formulae II and III.

The product prepared from 10 grams of anhydride by Stobbe's method was taken up in warm caustic alkali and then acidified and allowed to stand for some time. The product was extracted with sodium carbonate thus obtaining 6 grams of lactones and 3.2 grams of an acid which was apparently 1-phenylnaphthalene-2,3-dicarboxylic acid. This acid was boiled for a few minutes with acetic anhydride. After cooling, almost the entire quantity of acid was filtered off in the form of its anhydride, melting at 255°. The filtrate left a small quantity of residue on evaporation. This was recrystallized from 1 cc. acetic acid giving an additional small portion of the above anhydride. The acetic acid filtrate on evaporation left so little residue that it could not be identified. This residue would have contained any 1-phenylnaphthalene-1,2,3,4-tetrahydrodicarboxylic acid present in the reaction product because the anhydride of this acid is *easily soluble* in acetic anhydride while that of the unchanged substance is *very sparingly soluble.* This gives a very sharp separation of these two anhydrides and shows that the addition product is not formed.

The Oxidation of 1-Phenylnaphthalene-1,2,3,4-tetrahydrodicarboxylic Acid. —Stobbe states that he oxidized 1-phenylnaphthalene-1,2,3,4-tetrahydrodicarboxylic acid or its anhydride with chromic acid and that he obtained *o*-benzoylbenzoic acid. I obtained this acid several years ago among the oxidation products formed by using potassium permanganate in alkaline solution. This does not add any new fact to those used in determining the constitution of the 1-phenylnaphthalene-2,3-dicarboxylic anhydride as Michael and Bucher found that *o*-benzoylbenzoic acid is among the products obtained by oxidizing this anhydride directly. As Stobbe does not state the method of preparing the anhydride which he oxidized there is some doubt about this part of his work. If he used the product which he obtained from the reduction with zinc dust in acetic acid solution, he was presumably working with the above lactones (II and III). In a preliminary experiment, I found this mixture of lactones to oxidize to diphenyltetracarboxylic acid and ketone acids. Presumably they will also yield *o*-benzoylbenzoic acid under the proper conditions especially when oxidized in acid solution rather than in the alkaline potassium permanganate solution used in my case.

Allo-chrysoketonecarboxylic Acid.—In another article[1] Stobbe describes a compound under the name of allo-chrysoketonecarboxylic acid. He prepared the acid by adding 10 grams of 1-phenylnaphthalene-2,3-dicarboxylic anhydride to 500 cc. of cold concentrated sulphuric acid in the course of a day and then allowing the solution to stand two days. The product was then precipitated by throwing the solution on ice. The red acid thus obtained is identical with an acid which I noticed a number of years ago. In 1904, this acid was prepared in the following manner.

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[1] *Ber.*, **40,** 3383 (1907).

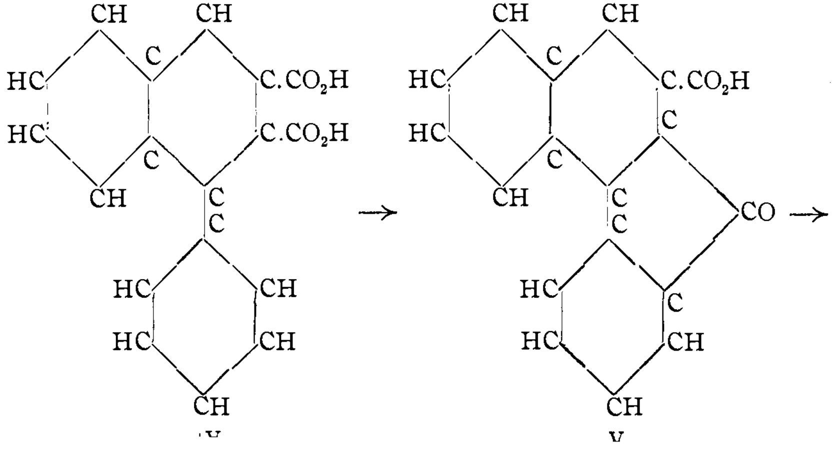
As the acid gives just as good results as the anhydride it was generally used.

Forty grams of 1-phenylnaphthalene-2,3-dicarboxylic acid were added to 200 cc. of concentrated sulphuric acid. The thick paste thus formed was heated to 100° over the smoky flame and kept at this temperature for a short time. The acid passes into solution quickly on shaking the flask, giving a solution free from suspended material. The red acid was separated by pouring the solution upon ice. The filtrate from the acid was perfectly colorless and the product was in excellent condition, the yield being 36 to 38 grams. The acid was dissolved in dilute potassium hydroxide solution, using only a slight excess of alkali. The sparingly soluble potassium salt crystallizes in long orange-colored needles as the solution cools. Further quantities of salt were obtained on concentration. On acidifying the final mother-liquor, about a gram of tarry acid separated. This decomposition product was no doubt due to having used too high a temperature in the preparation of the substance. In later experiments the temperature was kept lower and the liquid was filtered through glass wool to remove traces of suspended material which might be present. In this way the yield is practically quantitative, no decomposition products being formed. The acid was purified by crystallizing its alkali salts repeatedly from water containing a slight excess of alkali. The red acid obtained from this pure salt is very insoluble in water and very sparingly soluble in the ordinary organic solvents.

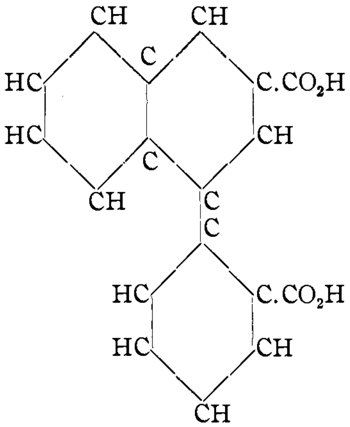
Analysis:

Calculated for $C_{18}H_{10}O_3$: C, 78.83; H, 3.65. Found: C, 78.33; H, 3.74.

This shows that the acid is isomeric with the 1-phenylnaphthalene-2,3-dicarboxylic anhydride and that the relation of these compounds is probably that shown by the following formulae (IV and V):



IV V



VI.

This view was confirmed by an analysis of the potassium salt which showed the acid to be monobasic. It melts at 288° *without decomposition*, forming a dark red liquid.

The description of this compound agrees in a general way with that given by Stobbe for his acid but there are a few important differences. He states that his compound melts at 285–6° "*unter lebhafter zersetzung.*" He also states that the sodium and potassium salts crystallize *without water of crystallization.*

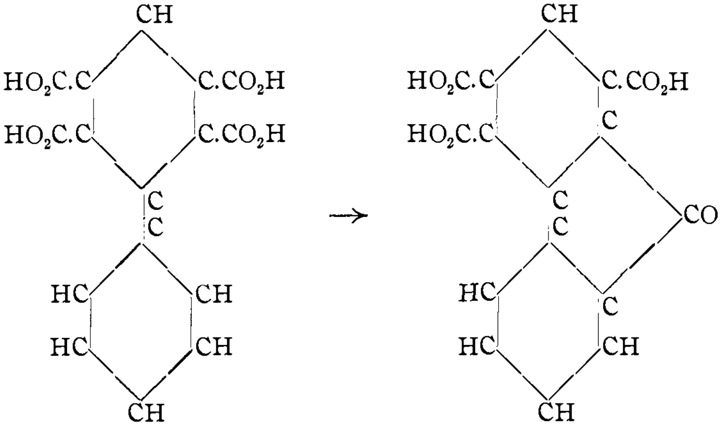
The acid obtained in this laboratory melts without decomposition and the potassium and sodium salts both contain water of crystallization. The former salt contains more than 13.5 per cent. of water. Several specimens of acid were prepared according to Stobbe's directions for comparison. All these melted at 288° *without decomposition* and their sodium and potassium salts *contained water of crystallization.* Mr. W. M. Gager found the sodium salt to lose about 7.6 per cent. of water on standing in the vacuum desiccator for several days and at 158° the loss was about 8.5 per cent. This result indicates that the sodium salt made from Stobbe's acid holds water of crystallization rather tenaciously. The potassium salt gives off much water when it is heated carefully in a test-tube. It is difficult to explain Stobbe's results in this case. Not only did the two acids give identical properties in this respect, but the melting points of the hydrazones, and of the ethyl esters were found to be identical. The conduct of the two acids is also the same when they are fused with caustic alkali, an acid which will be described later in this paper being obtained. As I could not detect the slightest difference in any of the experiments made with these acids it may reasonably be assumed that Stobbe's acid is identical with that obtained in a much less tedious way in this work.

As Stobbe has anticipated the publication of a portion of this work it seems advisable to publish the following outline of some of my results at this point.

When the allo-chrysoketonecarboxylic acid is heated with hydriodic acid in a sealed tube a colorless compound is formed. This substance is insoluble in cold sodium carbonate but dissolves readily in warm dilute caustic alkali. In acidifying the solution, the substance is precipitated and becomes insoluble in sodium carbonate. The compound is probably a lactone formed by the partial reduction of the ketone group.

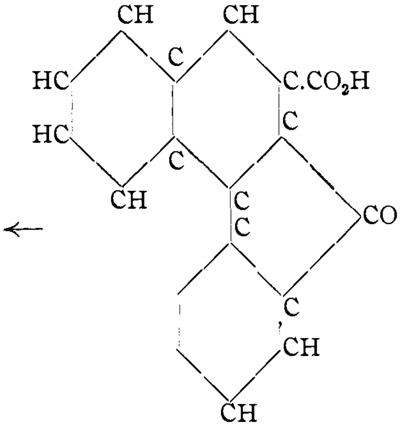
A portion of the potassium salt of the allo-chrysoketonecarboxylic acid was heated with barium hydroxide. The hydrocarbon produced has the odor and appearance of 1-phenylnaphthalene and it gave a good yield of *o*-benzoylbenzoic acid on oxidizing with chromic acid in acetic acid solution. This shows that the hydrocarbon is 1-phenylnaphthalene and its formation accords with the above constitution for the acid.

A number of years ago I obtained a yellow tribasic acid by the action of sulphuric acid on diphenyltetracarboxylic acid. There is no doubt that this acid is a diphenylenketonetricarboxylic acid formed by the removal of water from the former acid. Formulae VII and VIII show this relation.



VII. VIII.

This acid (VIII) has been thoroughly studied and can be identified very easily. Last year Mr. A. L. Claflin oxidized the red allo-chrysoketonetricarboxylic acid (IX) with potassium permanganate in alkaline solution. Among the products he found large quantities of the above diphenyleneketonetricarboxylic acid. Formulae IX and VIII indicate how this oxidation takes place and give further support to the constitution of these compounds. In this oxidation, an orange-colored acid and a white neutral substance behaving like a lactone are also formed.



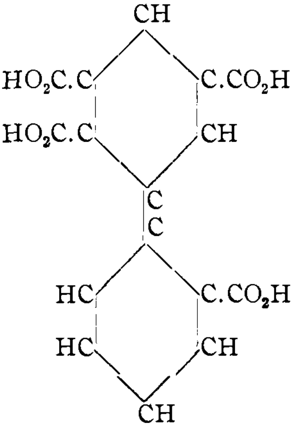
IX.

The action of caustic alkali on the allo-chrysoketonecarboxylic is also being studied. If this acid or better its potassium salt is fused with potassium hydroxide at the temperature of boiling naphthalene the red color very soon disappears. The white mass is taken up in water and then treated with hydrochloric acid. Practically a quantitative yield of a 1-phenylnaphthalenedicarboxylic acid is obtained, but this acid is entirely different from the 1-phenylnaphthalenedicarboxylic acid used in making the red acid. Mr. S. J. Beeber found that 0.1238 gram of the acid required 0.047 gram of potassium hydroxide for neutralization. This corresponds to a molecular weight of 295, the theory for an isomeric 1-phenylnaphthylenedicarboxylic acid being 292.

The acid crystallizes finely from glacial acetic acid in white crystals. The acid melts *without loss of water* at 288° and does not form an anhydride even when heated somewhat above its melting point. The carboxyl groups are therefore no longer in the *ortho* position. This transformation probably takes place according to the scheme shown above by formulae IV, V and VI.

This reaction gives a means of transferring the carboxyl group from the ortho position on one ring to the ortho position on the adjacent ring. The five-membered ring breaks practically quantitatively in such a way as to form this new acid (VI). If it broke the other way the original acid would be formed again, but as this acid could not be detected it is probable that this does not take place to any appreciable extent. This point is now being investigated.

The yellow diphenyleneketonetricarboxylic acid (VIII) shows a similar conduct on fusion with caustic alkali, a white diphenyltetracarboxylic acid being formed. This is isomeric with the acid (VII) from which the yellow acid was obtained and probably has the following structural formula.



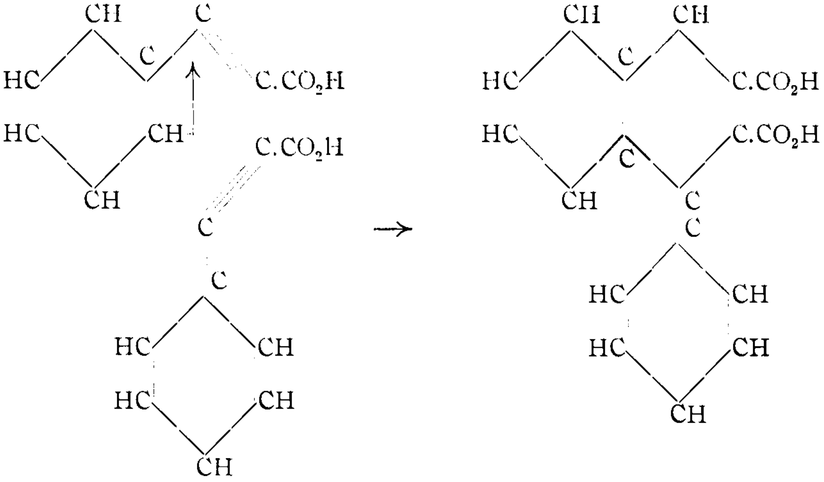
X.

It can be designated as diphenyl-2,3,5,6′-tetracarboxylic acid. In this case the ring again breaks practically quantitatively in such a way as to transfer the ortho carboxyl group to the corresponding ortho position on the other benzene ring. A very small quantity of the original acid which may be called diphenyl-2,3,5,6-tetracarboxylic acid was also obtained, the quantity being about one part for three hundred parts of the new acid. This shows that the ring breaks in the two ways but only to the extent of a trace in the latter case. These relations are shown clearly by formulae VII, VIII and X. The new acid can be separated very sharply from the original acid by means of the barium salts. On boiling a solution of these salts, the former *does not form a precipitate.*

During the past ten years, I have studied the action of acetic anhydride on a number of substitution products of phenylpropiolic acid. This work was carried on to show whether the reaction first observed by Michael and Bucher in case of phenylpropiolic acid is general or not. This involved the preparation of a number of new substituted phenylpropiolic acids and improving methods of preparation for those already known. Those prepared are as follows: Piperonylpropiolic acid, *o*-chlor-, *o*-brom-, *m*-nitro-, *m*-chlor-, *p*-nitro-, *p*-chlor-, *p*-brom-, *p*-iodo-, and *p*-methoxyphenylpropiolic acids. These all give anhydrides on heating with acetic anhydride. The acids from these anhydrides do not reduce an alkaline potassium permanganate solution (Baeyer's test). They are therefore saturated compounds, presumably derivatives of 1-phenylnaphthalene. This constitution has already been proved for most of the acids. This was done in some cases by transforming them into *diphenyltetracarboxylic acid*, and in other cases by oxidizing them to *benzene-*

pentacarboxylic acid. In fact, the 1-phenylnaphthalenedicarboxylic acid also yields this oxidation product thus confirming the constitution assigned by Michael and Bucher.

The above facts point very strongly to the conclusion that *phenylpropiolic acid and its substitution products show a strong tendency to polymerize, with the wandering of an ortho hydrogen atom, to phenylnaphthalene derivatives.* This is indicated in the simplest case by the formulae:



When phenylpropiolic acid is heated with acetic anhydride, the action takes place *explosively* if any large quantity is used. This acid also reacts with phosphorus oxychloride and it even passes into the naphthalene anhydride[1] when heated alone to 200°. Ruhemann and Meriman[2] obtained the same anhydride incidentally while working with the chloride of phenylpropiolic acid in pyridine solution. Pfeiffer and Möller[3] obtained the ester of the naphthalene acid by heating phenylpropiolic ester directly to 200°.

The above acids all give practically quantitative yields of anhydrides, thus giving a general method of synthesis for many naphthalene derivatives. It has the additional advantage either of showing the exact constitution of the substances formed or of limiting it to a very small number of possibilities. If the above generalizations are correct, it is also to be expected that substances which might pass into phenylpropiolic acid derivatives by molecular rearrangement, or by the loss of hydrogen by heating or by oxidation, would yield naphthalene derivatives. The oxidation of dibenzalsuccinic acid to 1-phenylnaphthalene-2,3-dicarboxylic anhydride

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[1] *Ber.*, **35**, 140 (1902).

[2] *J. Chem. Soc.*, **87**, 1389 (1905).

[3] *Ber.*, **40**, 3839 (1907).

and the formation of 1-phenylnaphthalene from the barium salt as observed by Stobbe[1] are excellent illustrations of the latter case.

In my work using acetic anhydride the two molecules of acid always condense to form anhydrides of *ortho* dibasic acids and therefore *1-phenylnaphthalenederivatives*. Under other conditions the polymerization might take place in the second possible way thus forming acids which have the phenyl group in the β-position. This point is now being investigated.

The above polymerization could probably not take place if both orthohydrogen atoms in phenylpropiolic acid were substituted. In order that this may be tested such substitution products are now being prepared. Considerable work has also been done on tetrolic acid and on propiolic acid. The former yields an anhydride of high molecular weight but the constitution has not yet been determined.

It is generally supposed that meta- and para-phthalic acids do not form anhydrides. Some facts noted in the course of this work lead me to the conclusion that the formation of anhydrides might take place in case of dibasic aromatic acids where the groups are not in the ortho position. Mr. W. C. Slade accordingly heated meta- and para-phthalic acids with acetic anhydride, finally distilling off at 200°. He obtained *quantitative yields of anhydride in each case.* By this procedure, it is no more difficult to prepare the meta- and para-anhydrides than those of ortho-acids. These two anhydrides titrate for the formula $[C_6H_4(CO)_2O]_x$ and the percentage of carbon and hydrogen also corresponds to this formula. They are insoluble in sodium carbonate solution but dissolve very easily in caustic alkali. When these solutions are treated with hydrochloric acid, the pure phthalic acids are recovered and the filtrates do not contain acetic acid. This shows that mixed anhydrides are absent. These anhydrides are almost insoluble in most organic solvents and take up water very readily in presence of solvents. These properties have thus far made all attempts to determine their molecular weights unsuccessful.

As the experimental work on a number of the lines of work mentioned in this paper is nearly complete, I should like to reserve this field until the results can be prepared for publication. This applies particularly to the following topics:

(1) The investigation of the oxidation products of 1-phenylnaphthalene-2,3-dicarboxylic acid.

(2) The study of the lactones (II and III) of this acid.

(3) The action of sulphuric acid on these acids leading to the formation of substances like those represented by formulae V and VIII and their derivatives (VI and X).

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[1] *Ber.*, 40, 3 (1907).

(4) The polymerization of the above-mentioned propiolic acids.[1]

(5) The anhydrides of meta- and para-phthalic acids.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

METHYL MESOXALATE AND SOME OF ITS REACTIONS.

BY RICHARD SYDNEY CURTISS AND PAUL T. TARNOWSKI.

Received June 12, 1908.

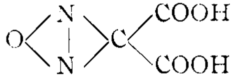
Several methods have been described for making methyl mesoxalate, but all are expensive in time and material, and leave much to be desired as to yield. Bouveault and Wahl[2] prepared ethyl and methyl mesoxalate by the reaction of nitrogen peroxide and ethyl and methyl isonitrosomalonate at a low temperature. Their yields were low, being between 34–40 per cent., most of their product being probably saponified by the action of water and the nitrogen peroxide used. Willstätter and Hottenroth[3] prepared the substance by heating methyl bromnitromalonate in a distilling flask. The distillate consisted of anhydrous methyl mesoxalate which, with water, gave methyl dihydroxymalonate.

In the different experiments tried with the oxides of nitrogen and malonic esters various products have been obtained.

Conrad and Bischoff[4] made ethyl isonitrosomalonate by treating the sodium salt of ethyl malonate in alcoholic solution with the red oxides of nitrogen.

Bouveault and Wahl[5] made methyl isonitrosomalonate by passing a current of methyl nitrite through a methyl alcohol solution of the sodium salt of methyl malonate P. T. Muller[6] made the same product by saponifying a methyl alcohol solution of nitrosocyanacetic ester with dry hydrochloric acid gas.

Traube[7] treated malonic ester with nitric oxide in presence of sodium ethylate and formed what he called oxazomalonic acid,



One of us[8] treated ethyl malonate with nitrous anhydride at a low

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[1] Mr. Dolt has just noticed that a specimen of piperonylpropiolic acid on exposure to light lost the power of reducing alkaline permanganate. This may prove to be the same naphthalene acid he obtained on heating with acetic anhydride.

[2] *Bull. soc. chim.* [3], **29**, 963.

[3] *Ber.*, **37**, 1781.

[4] *Ann. Chem.* (Liebig), **209**, 211.

[5] *Bull. soc. chim.*, **29**, 96.

[6] *Ann. chim. phys.* [7], **1**, 536.

[7] *Ber.*, **28**, 1795.

[8] Curtiss, *Am. Chem. J.*, **35**, 477.