

solutions of lactic, benzoic and salicylic acids and some other substances of more or less poisonous nature. Gasoline, benzene, esters of organic acids, ordinary ether, acetone, volatile oils and most other substances leave permanent disagreeable flavors.

Deglet Noor dates do not yield satisfactorily to these methods but can be made palatable and, if sufficiently mature, will yield fruit of fair quality when subjected to the judicious use of ethyl nitrite vapor. A small amount of this reagent ( $\frac{1}{4}$  to  $\frac{1}{2}$  cc. of 20 per cent. solution for every 1000 cc. of space enclosed) will finally render the tannin insoluble without discoloring the date badly or imparting any noticeable flavor.

It is anticipated that the application of these methods will prevent much of the enormous loss from souring which is experienced at present during unfavorable weather. Artificially ripened dates do not sour so readily as the fruit ripened on the tree and remain much freer from insects.

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## THE ACIDS OF THE PHENYLPROPIOLIC SERIES AND THEIR CONDENSATION TO NAPHTHALENE DERIVATIVES.<sup>1</sup>

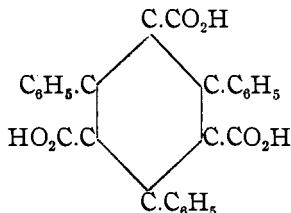
BY JOHN E. BUCHER.

Received December 9, 1909.

In an investigation of the action of acetic anhydride on acids of the acetylene series in 1895, Michael and Bucher<sup>2</sup> obtained the anhydride of a new acid from phenylpropionic acid. Three years later,<sup>3</sup> after a thorough study of the compound, they proved it to be the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid. It was found to have the composition corresponding to the formula  $C_{18}H_{10}O_2$  and a molecular weight of 274.

This corresponds to the composition of a phenylpropionic anhydride  $(C_6H_5C \equiv C.CO)_2O$ , but the acid obtained from it was found to be saturated and entirely different from phenylpropionic acid. This structural formula evidently does not represent its constitution.

It seemed probable that three molecules of the acid might have polymerized to triphenyltrimesic acid in a manner analogous to the for-



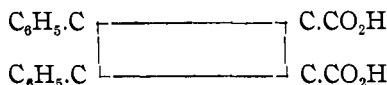
<sup>1</sup> Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 14, 1909.

<sup>2</sup> *Ber.*, 28, 2511 (1895).

<sup>3</sup> *Am. Chem. J.*, 20, 89 (1898).

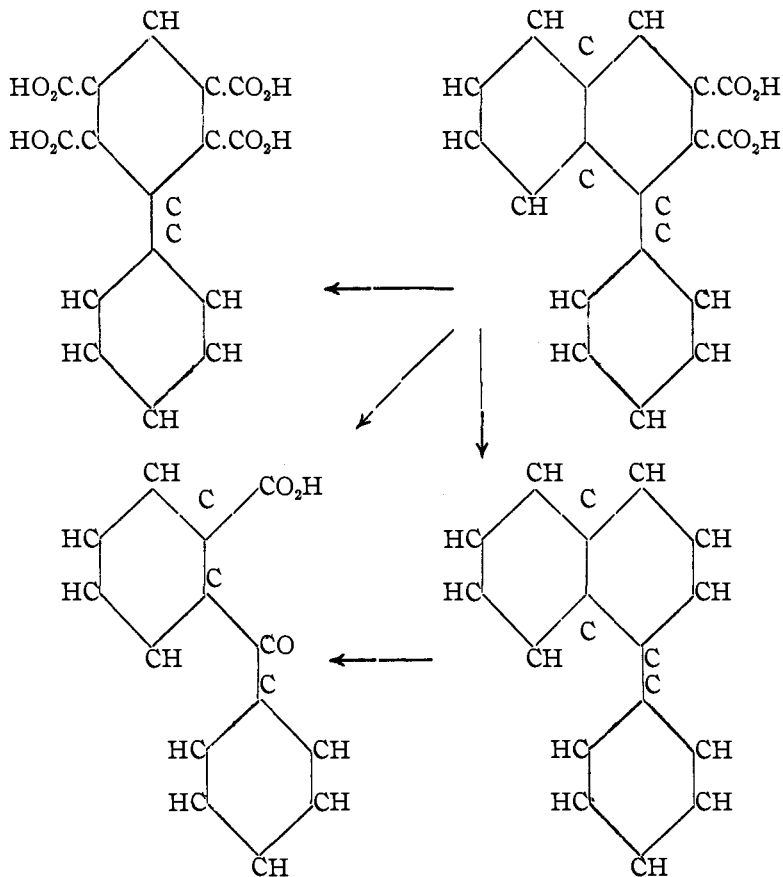
mation of benzene from acetylene. The resulting acid was found to be dibasic and to have only two-thirds of the required molecular weight. These facts showed conclusively that the compound is not the anhydride of triphenyltrimesic acid.

It was then thought possible that the compound might be the anhydride of diphenyltetrenedicarboxylic acid.



This acid would contain two carboxyl groups in the ortho position and it would be dibasic. One might expect benzil among the oxidation products of such an acid but many experiments failed to show the slightest trace of this substance. It was not possible to find any evidence in favor of the tetrene formula.

As none of these three formulas corresponded to the compound, it was evident that the polymerization of the phenylpropiolic acid must have proceeded in a very unusual manner.



They finally succeeded in isolating diphenyltetracarboxylic- and ortho-benzoylbenzoic acids from its oxidation products and in preparing its hydrocarbon. The hydrocarbon was also oxidized to orthobenzoylbenzoic acid. The preceding formulas show these transformations.

These facts can only be explained by the above constitutional formula and the compound is therefore the anhydride of 1-phenyl-2,3-naphthalenedicarboxylic acid.

Later, several investigators who evidently had overlooked the above work obtained this compound. Basing their reasoning on insufficient experimental evidence, they described the substance first as the anhydride of triphenyltrimesic acid and afterwards as that of diphenyltetrenedicarboxylic acid, representing structural formulas which had already been shown to be untenable by Michael and Bucher. For example, Lanser<sup>1</sup> obtained the compound by heating phenylpropionic acid with phosphorus oxychloride, and assigned the formula  $C_{54}H_{30}O_8$  for triphenyltrimesic anhydride without making molecular weight determinations.

A little later Manthey<sup>2</sup> determined the molecular weight thus showing the formula to be  $C_{18}H_{10}O_8$  and that the constitution must be different from that assigned by Lanser. This evidence together with the fact that the acid contains the two carboxyl groups in the ortho-position, led him to assign the tetrene formula.

In a later paper, Lanser and Halvorsen<sup>3</sup> acknowledge the correctness of Manthey's experimental work and they also accept the tetrene formula. The reactions which they study would, however, apply equally well to other ortho-dibasic acids.

Ruhemann and Meriman<sup>4</sup> also obtained the anhydride in studying the action of phenylpropionyl chloride on acetone in pyridine solution. They proved the identity of their compound with that of Lanser and regarded it as a terene compound as they did not investigate its constitution.

Michael<sup>5</sup> next showed that the compound described by these investigators is 1-phenyl-2,3-naphthalenedicarboxylic anhydride. He proved this by preparing a specimen by Lanser's method and finding it identical in every respect with a specimen prepared by the method of Michael and Bucher.

Recently, Stobbe<sup>6</sup> obtained this anhydride by the action of light on dibenzalsuccinic anhydride. Failing to get diphenyltetracarboxylic acid by direct oxidation but obtaining ortho-benzoylbenzoic acid, he claimed to have shown the truth of the naphthalene formula of Michael and Bucher for the first time.

These investigators<sup>7</sup> showed that his failure to get the diphenyltetracarboxylic acid was due to incomplete oxidation<sup>8</sup> and that they had

<sup>1</sup> *Ber.*, 32, 2478 (1899).

<sup>2</sup> *Ibid.*, 33, 3083 (1900).

<sup>3</sup> *Ibid.*, 35, 1407 (1902).

<sup>4</sup> *J. Chem. Soc.*, 87, 1389 (1905).

<sup>5</sup> *Ber.*, 39, 1908 (1906).

<sup>6</sup> *Ibid.*, 40, 3372 (1907).

<sup>7</sup> *Ibid.*, 41, 70 (1908).

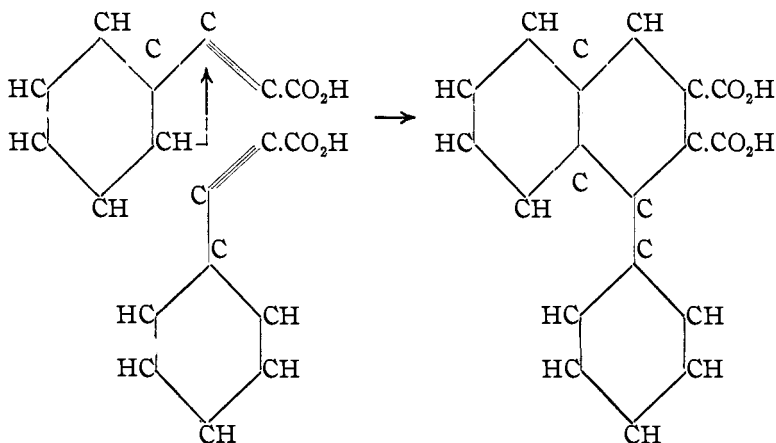
<sup>8</sup> *THIS JOURNAL*, 30, 1246 (1908).

noticed the formation of ortho-benzoylbenzoic acid by the *direct* oxidation<sup>1</sup> of the anhydride as well as from the hydrocarbon.

Pfeiffer and Möller<sup>2</sup> have polymerized phenylpropionic ester to the ester of 1-phenyl-2,3-naphthalenedicarboxylic acid by simply heating to 200°. They point out that aromatic acetylene derivatives may thus be polymerized to naphthalene derivatives without the use of condensing agents. The earlier work of Lanser also shows this since Michael has shown that the so-called triphenyltrimesic acid is really a naphthalene derivative. Lanser obtained the anhydride of this acid by heating phenylpropionic acid to a temperature above 200°. Pfeiffer and Möller's work, however, illustrates the additional fact that anhydride formation is not essential for this naphthalene condensation.

I have confirmed Lanser's experiment and have been able to get a much better yield of the ester of the naphthalene acid than Pfeiffer and Möller got. In my experiment, however, the phenylpropionic ester was polymerized by heating it with acetic anhydride instead of heating it alone.

These investigations show that phenyl propionic acid and its ester or chloride can be polymerized in a number of different ways to naphthalene derivatives but that the original method of Michael and Bucher which gives a quantitative yield is still the best. The following formulas indicate how this change takes place:



This work has been continued in this laboratory for a number of years in order to determine whether this transformation is general or not. Besides phenylpropionic acid, eleven of its substitution products have been examined thus far and in every case they polymerized, on heating with acetic anhydride, to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic anhydride. The facts thus far obtained justify the statement<sup>3</sup> that *phenylpropionic acid and its substitution products show a strong tendency to polymerize, with the wandering of an ortho hydrogen atom, to phenyl naphthalene derivatives.*

<sup>1</sup> *Am. Chem. J.*, 20, 112 (1898).

<sup>2</sup> *Ber.*, 40, 3839 (1907).

<sup>3</sup> THIS JOURNAL, 30, 1262 (1908).

In fact, this kind of polymerization is the only form which has been thus far obtained from aromatic propiolic acids.

In this work much time was spent in preparing the aromatic propiolic acids as it was usually necessary to either prepare new compounds or else to improve the methods of preparation of acids which were already known. In most cases methods were found by which these interesting acids could be prepared readily from comparatively inexpensive materials—providing that suitable precautions were observed.

Phenylpropiolic acid was prepared in the usual way from cinnamic acid by making cinnamic ester dibromide. It is well known that alcoholic potash converts this into a mixture of the salts of allo-bromocinnamic acid and bromocinnamic acid and that the latter is easily converted into phenylpropiolic acid by the loss of hydrobromic acid. The former acid is so stable, however, that it is not practicable to convert it into phenylpropiolic acid directly by further heating with alcoholic potash. It can, however, be converted into the isomeric acid by simply heating it. This acid can then be converted, in turn, into phenylpropiolic acid. This change of the labile bromo acids into the corresponding isomeric acids was found to be quantitative in several cases. In the case of the allo-bromocinnamic acid it was noticed that when it was heated with acetic anhydride to 100° its own anhydride was produced but at a higher temperature this was transformed into the bromocinnamic anhydride. The latter could then be transformed into phenylpropiolic acid. From this, it is evident that it is not necessary to use pure phenylpropiolic acid in this work. It generally seemed desirable, however, to separate the acids first. A very good way of doing this is to crystallize them from carbon disulphide or from carbon tetrachloride. In this way it is possible to separate much of the phenylpropiolic acid from the more soluble allo-bromocinnamic acid.

In some other cases, the potassium salts of the propiolic acids were found to be very sparingly soluble in the alcoholic potash, thus yielding the pure acids at once. In all cases the potassium salts of the labile bromocinnamic acids were found quite soluble while the ammonium salts of the isomeric acids were very sparingly soluble. These properties were found very useful in separating the resulting phenylpropiolic acids from these labile substituted bromocinnamic acids which were formed.

The meta- and para-nitrophenylpropiolic acids can be prepared from the corresponding nitrobenzoic aldehydes by Perkin's synthesis. In some other cases Claisen's synthesis was found preferable to that of Perkin.

It was also found that the ortho- and para-nitrophenylpropiolic acids could be converted into the corresponding halogen acids by means of the diazo reaction.

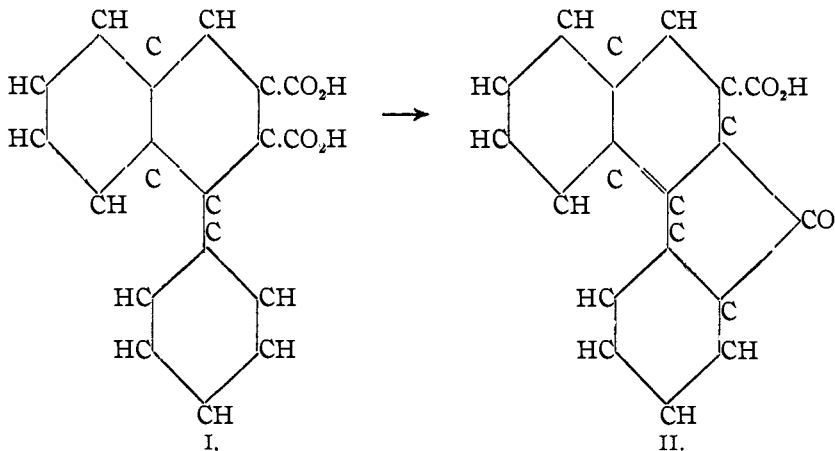
Besides phenylpropiolic acid, the following substitution products were prepared: Piperonylpropiolic acid, *o*-chloro-, *o*-bromo-, *m*-nitro-, *m*-chloro-, *p*-nitro-, *p*-chloro-, *p*-bromo-, *p*-iodo-, *p*-methoxy-, and *p*-methylphenylpropiolic acids. These all polymerize readily to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic anhydride when they are heated with acetic anhydride. In the earlier work it was found very difficult to prove this constitution for these products. The method used in case of the first compound has already been described. The meta- and para-nitro compounds were oxidized and then converted into diphenyltetracar-

boxylic acid thus showing them to be naphthalene derivatives. By means of the diazo reaction, they were then converted into the halogen derivatives identical with those obtained by direct polymerization. This showed the latter to have the same constitution. The constitution of the product from the para-methylphenylpropionic acid was established by oxidizing it to a diphenylpentacarboxylic acid. In more recent work the very efficient method of oxidizing to benzenepentacarboxylic acid described below was used. By means of this method, which depends on the catalytic action of manganese nitrate in fuming nitric acid, eleven of these acids were oxidized to benzenepentacarboxylic acids, thus confirming the naphthalene constitution which had previously been assigned for some of the substances.

The following description gives an idea of some of the transformations which these substances undergo: They are all ortho-dibasic acids from which water splits out easily on heating. In fact, the first acid obtained is partially converted into its anhydride even on crystallizing it from only moderately heated glacial acetic acid. In this way, I obtained eight grams of the anhydride from twenty grams of the acid. This loss of water in crystallizing the acid from hot solvents led to the statement, made in the first description, that the acid passed into the anhydride spontaneously. This statement was corrected in a later paper by Michael. All of these acids have this general property and some of them, as well as their oxidation products, may show properties similar to those noticed by Orndorff in the case of tetrachlorophthalic acid.

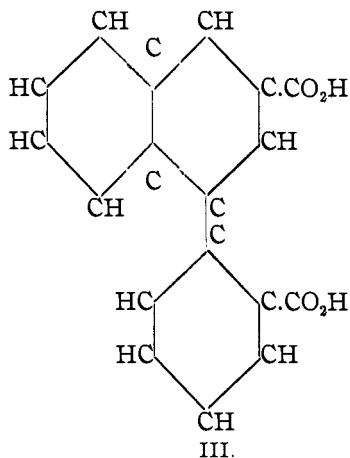
The acids all necessarily contain a carboxyl group with both ortho positions substituted. According to V. Meyer's observations one might expect difficulty in esterifying these acids. This was found to be the case, little or no neutral ester being found, on heating the substances with alcohol and sulphuric acid under the usual conditions. If more sulphuric acid is used and the heating continued for a longer time from 40 to 60 per cent. of neutral ester may be obtained.

Sulphuric acid converts the 1-phenyl-2,3-naphthalenedicarboxylic acid into red allo-chrysoketonecarboxylic acid.



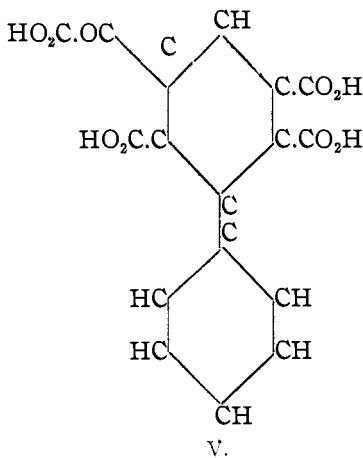
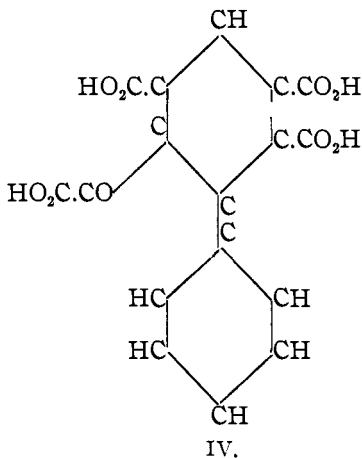
When this red acid is heated to  $218^\circ$  with potassium hydroxide, it is

changed practically quantitatively into a new 1-phenylnaphthalenedi-carboxylic acid.



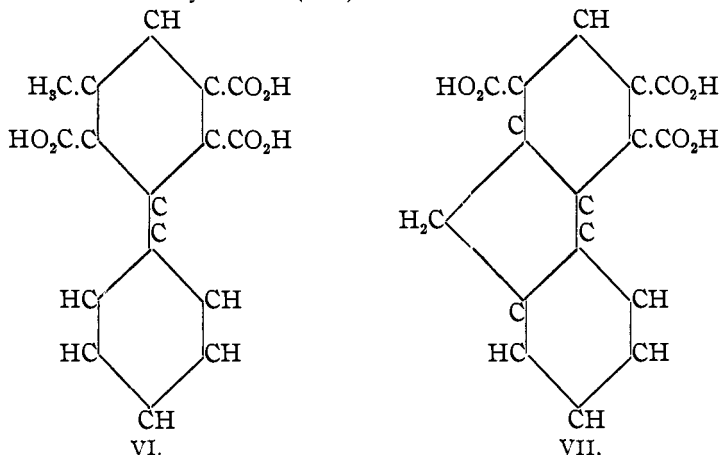
Formulas I, II and III show a method of transferring a carboxyl group from the ortho position on one ring to the corresponding position on the other ring. When the new acid (III) is heated with sulphuric acid, a new red acid different from the allochrysoketonecarboxylic acid (II) is obtained.

The oxidation of these naphthalene acids in alkaline potassium permanganate solution has already been described. The yield of diphenyl-tetracarboxylic acid is usually small, since the intermediate ketonic acids are very stable towards alkaline potassium permanganate.



These ketonic acids are very easily oxidized to diphenyltetracarboxylic acids when the solution is acidified. Formulae I, IV, V and VIII indicate these reactions. These acids are obtained in the form of sirup-like solutions and they resemble phthalonic acid closely. Heated with caustic alkalis, they yield diphenyltricarboxylic acids and oxalic acid.

On reduction with hydriodic acid, the *meta*-glyoxylic acid (V) first yields methyl-diphenyltricarboxylic acid (VI) which then reduces at a higher temperature to a methylfluorene-carboxylic acid. The isomeric *ortho*-glyoxylic acid (IV), even at the boiling point of hydriodic acid, reduces to a fluorene-tricarboxylic acid (VII).



This shows the ease with which diphenylcarboxylic acids close the ring to form fluorene derivatives. The same tendency is shown by the action of sulphuric acid on diphenyltetracarboxylic acid (VIII) in forming the yellow diphenyleneketone-tricarboxylic acid (IX), which can be reduced to the acid represented by formula VII. I have found this closing of the ring on heating to  $100^{\circ}$  with sulphuric acid, to take place when all the carboxyl groups were on the same ring but generally not when the carboxyl groups were on different rings. In diphenyleneketone-carboxylic acids of the general form IX, the ring is broken in such a way, on heating with potassium hydroxide, that the carboxyl group is transferred from the *ortho* position on one ring to the corresponding *ortho* position on the other.<sup>1</sup> In this case, about 299 parts out of 300 are changed in this way—making the process practically quantitative. The following formulas show these changes.

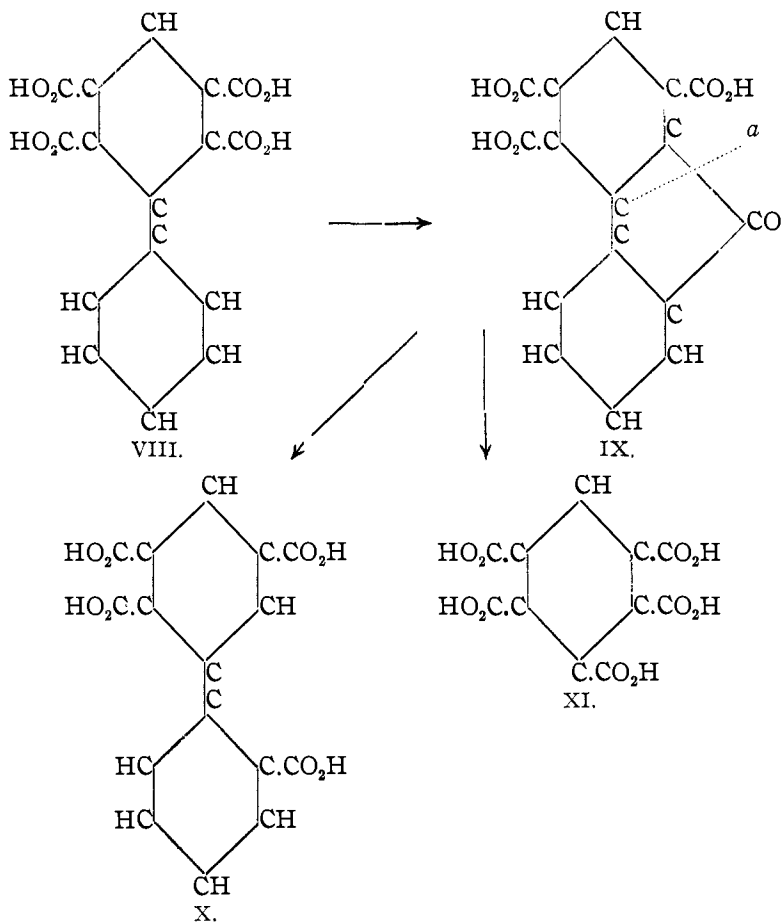
The very sharp breaking of the ring at *a* in formula IX and in the similar case of the red acid (II) indicates a tendency to remove the carboxyl groups as far as possible from each other and suggests the possibility of its giving a means of testing the constitution of the resulting acid. For example Bamberger and Hooker,<sup>2</sup> after heating a yellow diphenyleneketone-dicarboxylic acid from retene with caustic alkali, represent the resulting white diphenylenetricarboxylic acid as having the three carboxyl groups on the same ring. This seemed scarcely possible in view of the above facts and an examination showed the acid to have a different structure.

The yellow diphenyleneketone-tricarboxylic acid (IX) also furnishes a means of oxidizing these 1-phenyl-2,3-naphthalenedicarboxylic acids or diphenylpolycarboxylic acids (like I and VIII) to benzenepentacar-

<sup>1</sup> THIS JOURNAL, 30, 1261 (1908).

<sup>2</sup> *Ann.*, 229, 159 (1885).





boxylic acids. The latter acid (VIII) is very stable towards alkaline potassium permanganate as on heating for six weeks I recovered 28 per cent. of unchanged acid and could not isolate any benzenepentacarboxylic acid. The yellow acid (IX), however, decolorized the theoretical quantity of permanganate in less than two hours. The very soluble acid product was not completely oxidized but it yielded benzene for the hydrocarbon. Many experiments were made in attempting to complete the reaction but without success. Even heating on the water bath with fuming nitric acid did not aid very much. A small quantity of manganese nitrate was then added to the hot nitric acid. *Brisk effervescence began at once and in a few moments pure benzenepentacarboxylic acid separated from the liquid.* The yield in this experiment was about 90 per cent. of the theory. The manganese nitrate is evidently a very efficient catalytic agent in this case. This method was also applied to the acids without first converting them into ketone derivatives, and, in eleven cases out of the twelve tested, benzenepentacarboxylic acid was found. Not only does this give a very powerful method for determining constitution but

it gives a very easy method of preparing the hitherto almost inaccessible benzenepentacarboxylic acid. It also serves for the preparation of other benzene polycarboxylic acids. Bamberger and Hooker's diphenyleneketonedicarboxylic acid from retene can be oxidized in a few hours to two isomeric *benzenetricarboxylic* acids, thus showing that the constitution given for retene and all its derivatives is incorrect.

The above work dealing with the action of acetic anhydride led to the supposition that anhydrides<sup>1</sup> might be prepared from *meta*- and *para*-phthalic acids and their substitution products. On trying the experiment it was found that such anhydrides could be obtained quantitatively by heating a solution of the acid in acetic anhydride to 200° until the excess of reagent was distilled off. These products apparently have a very high molecular weight. A preliminary determination, in nitrobenzene by the boiling point method, for the anhydride from chloroterephthalic acid,  $[C_6H_3Cl(CO)_2O]_x$ , indicates that it may be as high as 1500 or 2000.

A part of this work has been carried on with the aid of my students and I wish especially to acknowledge the valuable assistance of G. F. Parmenter, N. A. Dubois, V. S. Babasinian, M. L. Dolt, W. C. Slade and F. Keyes.

The more important results of this work thus far are as follows:

1. Satisfactory methods for the preparation of a number of aromatic propiolic acids.
2. The polymerization of these acids to derivatives of 1-phenyl-2,3-naphthalenedicarboxylic acids—giving a quantitative method of synthesis.
3. Syntheses of acids of the diphenyl, fluorene and diphenyleneketone series and a study of their characteristic reactions.
4. Syntheses of benzenepentacarboxylic acid and other benzene-polycarboxylic acids.
5. The determination of the constitution of retene and its derivatives.
6. The preparation of anhydrides from *meta*- and *para*-phthalic acids and their substitution products.

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## CATALYSIS ON THE BASIS OF WORK WITH IMIDO ESTERS.<sup>2</sup>

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Received December 2, 1909.

I shall not attempt to discuss to-day the general subject of catalysis but shall use the short time rather to present briefly some results<sup>3</sup> in certain lines of our work which seem to shed some light on three fundamental points of interest in catalysis, namely, on the questions how in

<sup>1</sup> THIS JOURNAL, 30, 1263 (1908) and 31, 1319 (1909).

<sup>2</sup> Presented at the Second Decennial Celebration of Clark University, Worcester, Mass., September 15, 1909.

Certain parts of the work are still being carried out—as indicated below—and for such parts this report is preliminary to a final one. Complete discussion of the several parts lay outside the limits of this paper and will be brought in later special reports.