XLV.—On the Action of Hyponitric Anhydride on Organic
Bodies.

By Albert R. Leeds, Ph.D.

[Second Paper.]

In a preceding paper (Journal American Chemical Society,
2, 277) I have given the results which were obtained when hypo-
nitric anhydride was made to act at various temperatures upon ben-
zene, naphthalene and cymene. My object in the present paper is to
present, in conformity with the promise made at that time, the
results of the action of hyponitric anhydride upon a variety of other
organic bodies.

IV.—ACTION UPON TOLUENE.

In the latter part of May, 250 grms of toluene were treated with
the anhydride until the product ceased to increase in weight. It
was then poured from the five flat evaporating dishes, in which it
had been hyponitrified, into a flask, and left with only a sheet of
filter paper tied over the mouth of the flask, until the end of the fol-
lowing September. By this time all smell of the excess of dissolved
anhydride had diffused off, and a red oil remained, with numerous
large white crystals at the sides and bottom of the flask. These
were filtered off together with some adherent yellow solid matter,
and on examination proved to be oxalic acid. To get rid of the
oxalic acid the entire mass was dissolved in hot water, from which
a large crop of crystals separated on cooling, the oxalic acid, togeth-
er with a yellow coloring matter, going into solution. The crystals
thus obtained were repeatedly crystallized out of boiling water, until
they became almost colorless. Afterwards, being small and not well
defined, they were crystallized out of alcohol, benzene and chloroform,
but not with much greater success. The latter solvent afforded them
in nodular masses, composed of white translucent leaflets, which pol-
arized under the microscope. Considerably below 200° the crystals
begin to subline, and are slowly volatilized without melting or un-
dergoing decomposition, even when the temperature is raised as high
as 230°. The product, purified as far as possible by repeated crys-
tallization from boiling water, was accordingly transferred to a re-
tort and kept in the air bath at the temperature of 170°, until all the
crystalline substance was sublimed over. The crystals thus obtained
were readily soluble in hot water, alcohol, benzene and chloroform,
but in cold water almost insoluble.

On analysis they were found to contain:

	I.	II.
Carbon	52.33	53.23
Hydrogen	3.75	5.08

These figures closely approximate to the composition of dioxy-benzoic acid, $C_6H_3(OH)_2.COOH$, the discrepancy being in a somewhat low percentage of carbon. In order to ascertain whether a different result could be obtained by further purification of the substance, it was once more sublimed, this time at a temperature of 220°, twice dissolved in boiling water, allowed to cool after each solution, filtered, washed and dried over sulphuric acid.

0.1979 grm of the substance yielded on combustion, 0.3888 grm carbonic acid, and 0.0691 grm water, corresponding to

	Found.	Theory.
Carbon	53.58	54.54
Hydrogen	3.88	3.89

This would add a fifth to the four previously known of the six possible modifications of dioxybenzoic acid. From three of these, protocatechnic acid, oxysalicylic acid and the dioxybenzoic acid (1:2:4), it differs both in its melting point and in not yielding a coloration with ferric chloride.

It agrees most nearly with the modification, which has been obtained by Barth and Senhofer*. By heating benzoic acid along with sulphuric acid and phosphoric anhydride to 250°, in sealed tubes, they produced a disulphobenzoic acid, the potassium salt of which, when melted with potash, yielded the modification of dioxybenzoic acid referred to. But the new modification differs from this body by its not forming a hydrate when crystallized out of hot water. It is anhydrous, whilst the acid of Barth and Senhofer in the air-dried state, contains $1\frac{1}{2}$ molecules of water. Unlike this acid, which melts with decomposition at 222°, it does not melt, but begins to sublime at 170°, and may be sublimed without undergoing change, even when the temperature is raised as high as 230°. The acid of Barth and Senhofer, when heated with strong sulphuric acid, dissolves to a red liquid that deposits a green powder on the addition of water. In the case of the new acid, its solution in sulphuric acid is not colored. It forms readily soluble salts with the alkalies, alkaline earths and with lead. Its silver salt, which while somewhat soluble in water, is the least soluble of the salts thus far made, crystallizes in thin transpar-

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* *Ann. Chem. Pharm.* **159**, 217; **164**, 109.

ent plates with a silky lustre. Unlike the silver salt of the acid obtained by Barth and Senhofer, which contains 1 molecule of water of crystallization, this salt is anhydrous. Finally, the acid of Barth and Senhofer is described as crystallizing in prisms or thin needles, whilst the new acid, whether crystallized by sublimation or from solution, forms aggregates of small leaflets. From a consideration of all of these characteristic differences, it would appear that the new substance is one of the two remaining possible, but hitherto not isolated, modifications of dioxybenzoic acid.

The original oil, from which the oxalic and dioxybenzoic acids had been separated by filtration, on standing formed two layers, the lower of which a much lighter red color than the upper layer. These two portions were divided by a separating funnel, and distilled. The denser yielded mostly nitric acid, after which a small portion of oil came over, and lastly, a white crystalline sublimate. The lighter yielded first an oil and then a crystalline body ; both distillates apparently being identical with those obtained from the denser liquid. The amount of the crystalline product being small, it was feared that it could not be obtained in a pure condition from the large quantities of oil with which it was associated. All the distillates were therefore reunited and distilled with water. The oil came off plentifully along with the steam, at first of a light yellow color, and later on, as the distillation continued, of a yellowish-red to red color. On separating all the oil from the various portions of the distillate, and distilling it free from water, in a small retort, the temperature rose to $222°$ $-223°$, when it became constant, and most of the oil came off. Afterwards the thermometer rose to $228°-229°$, when it again became constant, and the remainder of the oil came over, leaving only a very small residue, consisting of a dark reddish oil behind. Both portions had exactly the same beautiful tint of straw-yellow color. But the latter, with the considerably higher boiling point, was thought to be a different substance from the oil boiling at $222°$, until its specific gravity was determined, which was 1.159. The specific gravity of orthonitrotoluene is stated to be 1.163, and both portions of the oil therefore were orthonitrotoluene.

As the oil was distilled off with the water in the original process of the purification, the residue became more and more solid, until finally, on cooling, the liquid became filled with crystals. These were purified by repeated crystallization from boiling water, in which they were readily soluble, until they were almost colorless. They were further purified by sublimation, the sublimed crystals

melting at 120°, which melting point, together with the white laminated appearance of the crystals formed by sublimation, and the characteristic odor given off on heating, proved the substance to be benzoic acid.

Finally there remained behind, after all the oil and benzoic acid had distilled over, a large amount of a very dark colored tarry residue. This was sublimed at a temperature of about 110°, yielding nearly 10 grms of beautiful light yellow crystals. These were needle-shaped, but clustered together so as to form feathery or arborescent crystals. Their solution in water was light yellow, staining silk permanently of the same color. No insoluble salt could be formed. After repeated sublimation, the melting point of the crystals was 109° to 110°, and since this is likewise the melting point of paradinitrocresol, $C_7H_6(NO_2)_2O$, the supposition first formed was that the new substance was no other than paradinitrocresol. The similarity in its dyeing and other properties, and its mode of derivation (paradinitrocresol being obtained by the action of nitrous acid on paratoluidine), gave to this supposition so strong a likelihood that it was abandoned only after repeated analyses. The first two analyses gave:

	I.	II.	Theory.
Carbon	39.26	39.60	42.42
Hydrogen	2.98	4.24	3.03
Nitrogen		14.19	14.14

A portion of the supposed paradinitrocresol, after resublimation, was crystallized out of its solution from alcohol. 0.2113 grm of this product gave 0.3016 grm carbonic acid and 0.0678 grm water, corresponding to

Carbon	38.92
Hydrogen	3.56

Two more analyses were made, with the result of showing that the new substance was not paradinitrocresol, $C_7H_6(NO_2)_2O$, but dinitro-orcine, $C_6H(CH_3)(NO_2)_2(OH)_2$, which differs from the former only in containing one more atom of oxygen. In other words, not only had two of the atoms of hydrogen in the toluene been replaced by NO_2, but it had been raised by oxidation to the condition of a derivative of orcine. Unexpected as was this result, yet it is fully confirmed, not only by these repeated analyses, but also by those made later upon the constitution of the salts. Comparison with dinitro-orcine, $C_6H(CH_3)(NO_2)_2(OH)_2$:—

	IV.	V.	Theory.
Carbon	39.99	38.55	39.25
Hydrogen...........	2.98	4.01	2.80
Nitrogen..	13.82		13.09

Dinitro-orcine has already been obtained by Stenhouse and Groves*, by the action of dilute nitric acid in the cold upon nitroso-orcine; strong nitric acid forms trinitro-orcine. But the physical and chemical characters of the body obtained by Stenhouse and Groves, are altogether different from those of this new modification derived from toluene. In the absence of present knowledge as to the relative orientation of the NO_2 group in the two bodies, I shall designate the former as α, the latter as β-dinitro-orcine. The melting point of the former, as determined by Stenhouse and Groves is 164°.5, that of the latter is 109° to 110°. The former crystallizes in deep yellow rhomboidal plates; the latter as bright yellow needles, when prepared by sublimation, and as golden yellow needles, when crystallized out of alcohol. The former is almost insoluble in cold water, the latter is slightly soluble in cold, very soluble in boiling water. The alkaline salts of α-dinitro-orcine are very soluble in water, difficult to crystallize, and orange-red in color. The same is true of the solubility of the corresponding salts of β-dinitro-orcine, but their color is golden yellow. The calcium and lead salts of β-dinitro-orcine crystallize in yellow needles, the silver salt in plates. While barium forms with dinitro-orcine two hydrated salts, one of which is normal, the other acid, β-dinitro-orcine forms only one, and that the normal salt. It crystallizes in long reddish-yellow needles, which have the property not shared by any other of the salts so far examined, of exploding violently when heated. It crystallized likewise from alcohol, but not so well as from water, forming groups or nodules of small needles.

An attempt was made to form two salts with toluidine, by bringing one and two molecules of toluidine in alcoholic solution, into combination with one molecule of β-dinitro-orcine likewise dissolved in alcohol. The salts which were formed in both cases, after recrystallization from alcohol, had the same melting point of 108°. Whilst both crystallized in small yellowish-red needles, that with two molecules of toluidine was somewhat the lighter in color. For this reason, both salts were redissolved in water, in which they are readily soluble. They crystallized out in needles of the same color, but

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* *Journ. Chem. Soc.*, 1877, 548.

much larger than those obtained from the alcoholic solutions.   The melting points of both substances still remained at 108°.   An analysis of that prepared with a solution of two molecules of toluidine, and recrystallized from water, demonstrated that it contained in chemical combination but one molecule, and that both substances were the same body, the normal tolnidine salt of dinitro-orcine or $C_7H_9N.C_7H_6(NO_2)_2O_2$.

0.1793 grm of the salt yielded 0.3566 grm of CO_2 and 0.0852 grm of water, corresponding to

	FOUND.	THEORY.
Carbon	54.24	54.72
Hydrogen	5.28	4.89
Nitrogen		9.12
Oxygen		31.27

The amide was prepared by reduction of the β-dinitro-orcine by means of tin and hydrochloric acid.   After complete reduction had been effected, the tin was precipitated by sulphuretted hydrogen, the stannous sulphide filtered off, and the filtrate evaporated to dryness. The amide was left as a dark reddish-brown powder.   Attempts made to obtain it in a crystalline form, by the use of various solvents and by sublimation, were unsuccessful.

In concluding this part of the subject, it should be mentioned that the aqueous solutions of β-dinitro-orcine and certain of its salts, dye silk a permanent and very beautiful yellow color.   Its ready preparation by the treatment of toluene with hyponitric anhydride, and its relatively large yield therefrom, may render its practical application in the arts of some future importance.

<center>XYLENE.</center>

250 grms of xylene, after treatment with hyponitric anhydride in the same manner as the toluene, at the expiration of a like interval of 5 months, were found to have yielded an abundant crop of large colorless crystals along with some adherent solid matter, and a supernatant yellowish-red oil.   No unaltered xylene remained.   The solid portion, by treatment with successive portions of water, was separated into oxalic acid, which had constituted the colorless crystals alluded to above, and another white crystalline body with a melting point, as determined after repeated crystallizations, of 192°–193°.   A combustion performed on 0.1537 grm of this latter substance yielded 0.3255 grm CO_2 and 0.0566 grm H_2O, from which it appears that its formula is identical with that of phthalic acid, $C_6H_4(COOH)_2$:—

	FOUND.	THEORY.
Carbon	57.75	57.53
Hydrogen	4.09	3.62
Oxygen		38.85

The oily portion was distilled with water, and the oil which came over in the distillate was purified by repeated distillation in a current of steam, until its boiling point became constant. This was at 234°, proving that the light yellowish-red oil thus obtained, was ortho-nitroxylene. On cooling, the water in the retort deposited crystals, which after being repeatedly recrystallized from boiling water, proved to be paratoluic acid. The insignificant amount of reddish solid residue finally left in the retort, was found to consist merely of paratoluic acid with a small amount of oil.

PHENOL.

The phenol was attacked by hyponitric anhydride with great energy and rapidly converted into a blackish mass. On boiling this with water, and filtering from the carbonized residue, the solution deposited crystals which, on recrystallization, proved to be picric acid. This was the only substance present; instead of obtaining, as in the case of the substances previously experimented upon, a mixture of nitrified and oxidized bodies.

ANILINE.

Aniline was likewise very energetically attacked by N_2O_4, and converted into a black semi-solid mass. When this was treated with hydrochloric acid a portion dissolved in the acid, and was again precipitated by potash. On attempting to subline the original nitrated product, a large amount of aniline was distilled off, but no crystalline sublimate was obtained. Another portion was prepared, and a portion subjected to very careful distillation, the temperature of the retort being kept at about 185°. A light red oil was given off at this temperature, which gradually became darker in color. After several hours the entire mass was carbonized, but no crystalline sub-limate came over. Another portion of the raw product was boiled with water and filtered while hot, and then, becoming turbid on cooling, was again filtered. It yielded a dark red liquid. This was evaporated to dryness, on the water bath, leaving a blackish solid residue. This residue was then redissolved in water, and again evaporated to dryness when it had lost most of its tarry properties, though it did not present a crystalline appearance. On heating, it

gave off only a few drops of oil until, the temperature having been raised very slow , to 174°, it gave a violent puff and carbonized.

Having failed to obtain from aniline any results by methods similar to those which had proved successful with the other substances experimented upon, various portions of the aqueous residue were dissolved in alcohol, ether, chloroform, hydrochloric and acetic acids. The chloroform appeared to answer best because it dissolved the smallest amount of the tarry matter, and from the solution some needles crystallized out. But they were in quantity too small to admit of their analysis, nor was a more successful result obtained when the entire aqueous residue from another portion of the nitrated aniline was treated in like manner. What, however, we had failed to do with care was apparently accomplished in one instance by accident. A portion of aniline, amounting to about 100 grms, was treated with hyponitric anhydride for a shorter period than usual, a considerable amount of the aniline being left unacted upon. On expelling the excess of aniline by boiling with water, a crop of crystals separated out at once from the cold aqueous solution. These crystals were repeatedly crystallized out of alcohol, until their melting point became constant at 123°. They were in the form of long needles, with a beautiful dark red color, and contained nitrogen; unfortunately only 0.0707 grm remaining after purification, for analysis. It gave 0.1883 grm CO_2 and 0.05 grm H_2O, corresponding to 72.63 per cent. of carbon, and 7.85 per cent. of hydrogen. Such a percentage of carbon could not be brought into harmony with any formula, and it was evident that the analysis was at fault.

It is useless to narrate the remaining unsuccessful experiments. On the supposition that a too long exposure to the hyponitric anhydride had, in all trials except the previous partly successful one, decomposed the nitro-derivatives first formed, various new portions of the aniline were treated with hyponitric anhydride for different periods, and the resulting products examined, but without success. My object in giving these details, at such length, is to assist any one who may in the future repeat these experiments. The properties and melting point of the body found differ widely from those of any of the nitranilines hitherto obtained, and there is little question of its being a new substance.

ORTHOTOLUIDINE, XYLIDINE, CRESOL.

The results arrived at with these bodies were still less satisfactory than those obtained with aniline. 100 grms of orthotoluidine (m. pt.,

199°) were treated with hyponitric anhydride for three hours, when the operation was discontinued, the toluidine apparently being com-pletely changed and converted into a black solid. This product was boiled with water, the solutions after cooling filtered and evaporated to dryness. A purplish-black residue remained with some minute leaf-like crystals. This was transferred to a retort, and the tem-perature raised very cautiously. No sublimate came off below 135°, and at this point the substance was decomposed with a puff, leaving only some carbonized matter behind. On attempting to dissolve out, by the use of solvents, any crystalline bodies present in the residues obtained from the solution of other portions of orthotolui-dine similarly nitrated, or to carry them over by distillation in a current of superheated steam, no results were obtained.

100 grms of xylidine, after nitration for four hours, and 100 grms of cresol, after nitration for twelve hours, were converted into blackish-red masses, which were treated in like manner with boiling water, and their aqueous solutions after filtration evaporated to dry-ness. Dark red residues were obtained from both substances, and these residues were decomposed at low temperatures when attempts were made to sublime them. Nor were any products obtained by the use of solvents, or by distillation in a current of steam.

ANTHRACENE.

Anthracene is converted by the action of hyponitric anhydride into anthraquinone. Along with the anthraquinone a small amount of red oil is formed, which is best removed by mechanical separation with filter paper, and by washing with ether. Since, in every other in-stance, besides a product of oxidation, some nitro or hydroxyl-deriva-tive had been obtained, it was thought that a different result might be arrived at by operating upon a solution of anthracene in glacial acetic acid. 50 grms of anthracene, dissolved in 400 c.c. of the acid, yielded, after saturation with N_2O_4, 58 grms of anthraquinone. The theoretical amount of anthraquinone was 58.3 grms. A little red oil was formed at the same time, but no hydroxylated or nitro-deriva-tive.

|		Oxides.	Nitro-derivatives.	Nitro-hydroxyl.	Hydroxyl-derivatives.
Benzene	C_6H_6	CO_2 $C_2H_2O_4.2H_2O$ C_6H_4O(M.P.215°)	$C_6H_3(NO_2)$	$C_6H_2(NO_2)_3OH$	$(C_6H_5.OH)$
Toluene	$C_6H_5.CH_3$	$C_2H_2O_4.2H_2O$	$o—C_7H_7(NO_2)$ (B.Pt., 222°)	$\beta—C_6H(CH_3)(NO_2)_2(OH)_2$ (M.Pt., 109°–110°)	$C_6H_3(CH_3)(OH)_2$ $C_6H_5.COOH$ $C_6H_3(OH)_2.COOH$
Xylene	$C_6H_4(CH_3)_2$	$C_2H_2O_4.2H_2O$	$o—C_8H_9(NO_2)$ (B.Pt., 234°).	?	$C_6H_4(CH_3).COOH$ $C_6H_4(COOH)_2$
Cymene......	$C_6H_4.CH_3.C_3H_7$	$(C_2H_2O_4.2H_2O)$	$\alpha—C_{10}H_{10}(NO_2)$	?	$C_6H_4(CH_3).COOH$
Naphthalene...	$C_{10}H_8$	$C_2H_2O_4.2H_2O$ $C_{10}H_4O_4$	$C_{10}H_7(NO_2)$ $\alpha—C_{10}H_6(NO_2)_2$ $\beta—C_{10}H_6(NO_2)_2$	? ? ?	$[C_6H_4(COOH)_2]$ $C_{10}H_4(OH)_4$?
Anthracene....	$C_{14}H_{10}$	$C_{14}H_8O_2$			
Phenol..	$C_6H_5.OH$			$C_6H_2(NO_2)_3OH$	

CONCLUSION.

By an examination of the accompanying table of products, it will be seen that in every case except in those of anthracene and phenol, oxalic acid was one of the substances formed. That this should have happened with anthracene was not to be expected, inas·much as anthracene is converted by direct oxidation into anthra·quinone. By an oversight, the fact of the production of oxalic acid from naphthalene was not mentioned in the original article, although its isolation and analysis were given at length in the original notes. In the case of cymene, the oxalic acid is enclosed in brackets to in·dicate that it was not isolated. The cymene was examined immedi·ately after nitration, the toluene and xylene not until after several months, during which long interval an opportunity had been afford·ed to the oxalic acid to separate in crystals.

The new oxygen derivative, C_6H_4O, obtained from benzene, *is not quinone*, $C_6H_4O_2$. Although in a brief abstract of my first article published in the *Berichte der deutsch. chem. Gesellschaft*, **13**, 1993, this substance is stated to be quinone, yet this statement is incorrect. It is expressly mentioned in my original paper, that the composition and the properties of the new substance conclusively establish that it is not quinone, but a monoxy·derivative of benzene.

The most striking phenomenon connected with the action of hyponitric anhydride upon the aromatic compounds, is the absence of uncombined water from among the products, and the formation of hydroxylated derivatives. The introduction of the hydroxyl group, in fact, is to be looked upon as the principal function of hyponitric anhydride in these cases. It is to be regarded, therefore, as an agent of quite a different sphere of application from nitric acid, which, under like circumstances, together with a certain amount of oxidation, acts chiefly by the introduction of the NO_2 group, water being eliminated. Not water, but nitrous oxide, N_2O, is given off when hyponitric anhydride is employed. No nitric oxide was found in the gas after it had acted upon the compound (benzene was the body more especially experimented upon in this connection), while *laughing gas was given off in great abundance.* This fact, together with the occurrence of the water of crystallization in the crystallized oxalic acid, which very slowly separated out of the mother liquid, is to be borne in mind in attempting to obtain, in a chemical equation, the numerous products actually formed. In the case of benzene, the following equation would be in harmony with what was actually ob·served:

$$6C_6H_6 + 13N_2O_4 = 3(C_2H_2O_4.2H_2O) + C_6H_4O + C_6H_5(NO_2) + C_6H_5.OH +$$
$$C_6H_2(NO_2)_3.OH + 6CO_2 + 7N_2O.$$
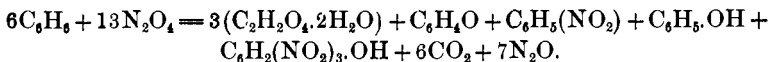
When nitric acid acts upon benzene, the reaction takes place in accordance with the familiar equation :

$$C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O.$$
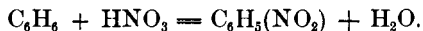
But the liberation of N_2O, when N_2O_4 acts upon the aromatic compounds, shows that a decomposition must occur represented by

$$N_2O_4 = N_2O + O_2 + O.$$
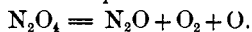
In other words, the fact that an uneven number of atoms of oxygen is set free shows that at the moment of their liberation, one at least of these atoms must be in its uncombined or nascent condition. And while it has been abundantly demonstrated that triatomic oxygen cannot oxidize the elements of water into the form of hydroxyl, it has been conclusively shown that nascent or monatomic oxygen can. This is strikingly shown in the oxidation of phosphorus in the presence of water, where the nascent oxygen necessarily set free in the course of oxidation of the phosphorus, not only oxidizes the oxygen present into ozone, but a portion of the water into hydrogen peroxide. So, likewise, if benzene be added to the water in which the phosphorus is undergoing oxidation in partial oxidation with air, the ozone reaction disappears, and under proper conditions a notable amount of phenol is formed. The details of this experiment will presently be made public.

The sequence of decompositions resulting from the action of hyponitric anhydride upon benzene would appear to be as follows :

(1.) $3C_6H_6 + 2N_2O_4 = 2C_6H_5(NO_2) + C_6H_5.OH + N_2O + H_2O + O.$

(2.) $C_6H_6 + O + O = C_6H_4O + H_2O.$
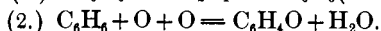
The water thus found appears to have been that essential to the formation of the crystallized oxalic acid. No uncombined water, as previously stated, was found among the products of the reaction.

The phenol was at once and entirely converted into picric acid, a change established by an independent research upon the deportment of phenol itself with hyponitric anhydride.

So likewise in the treatment of the toluene, no less than three hydroxyl derivatives were produced—benzoic acid, the new modification of dioxybenzoic acid, and orcine, which was afterwards converted into the β-dinitro-orcine. In other words, we have in the first case the conversion of the side chain into carboxyl; in the second, this conversion along with the replacement of two hydrogen atoms of the nucleus by hydroxyl; in the third, the side chain is unaffected, and only the two hydrogen nucleus atoms have suffered replacement.

Similarly the xylene lost not only one of its two methyl groups, forming paratoluic acid, but also both of the members of the side chain with the production of phthalic acid. In the case of cymene, however, the propyl group appeared to break down so much more readily than the methyl group, that the latter was protected from the oxidizing action, and the only hydroxylated derivative was paratoluic acid. But the most striking exemplification of this tendency to form hydroxyl derivatives was exhibited by naphthalene. Not only was the carboxyl group produced, with the generation of phthalic and oxalic acids (both of which changes might be looked upon as evidence of a similarity of action between hyponitric anhydride and nitric acid), but the new hydroxylated compound, tetroxynaphthalene, $C_{10}H_4(OH_4)$, was formed. In this body no less than four of the hydrogen atoms in naphthalene are replaced by hydroxyl. At the same time, the diquinone, $C_{10}H_4O_4$, was formed, in which four atoms of hydrogen are replaced by oxygen.

It is not improbable that both dioxynaphthalene, $C_{10}H_6(OH)_2$, and naphthoquinone, $C_{10}H_6O_2$, were first formed and afterwards converted into these higher derivatives. But of these, and of naphthol and of dioxynaphthoquinone, $C_{10}H_4O_2(OH)_2$, no evidence could be found in the final products.

XLVI.—DETECTION OF STARCH SUGAR MECHANICALLY MIXED WITH COMMERCIAL CANE SUGAR.

BY P. CASAMAJOR.

[Second Paper.]

In a previous communication on the same subject,* read before the American Chemical Society at the meeting of March, 1880, I gave several processes for the detection of starch sugar in commercial sugars. One of these consisted in adding to the suspected sugar a quantity of cold water, somewhat less than its own weight, and stirring the mixture for a few seconds. If starch sugar is present, it will be seen in the shape of white chalky specks.

Quite lately a sample of yellow refined sugar was given to me which was supposed to be adulterated by being mixed with starch glucose. By applying the test just mentioned, there seems to be left a few small chalky specks, which dissolved after standing a minute or two, making it very uncertain whether any starch glucose was present. Upon repeatedly trying the same test, the result was always doubtful.